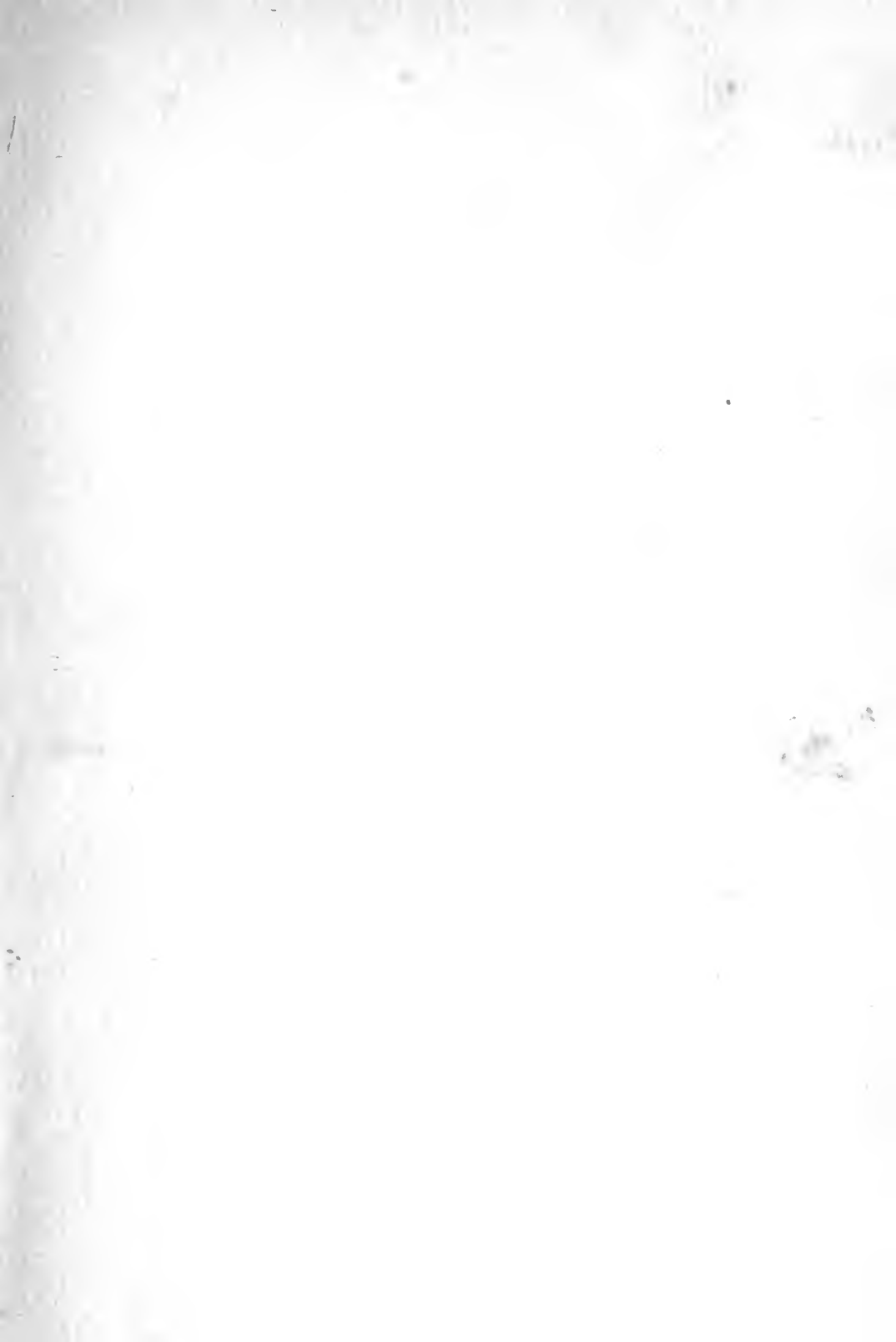


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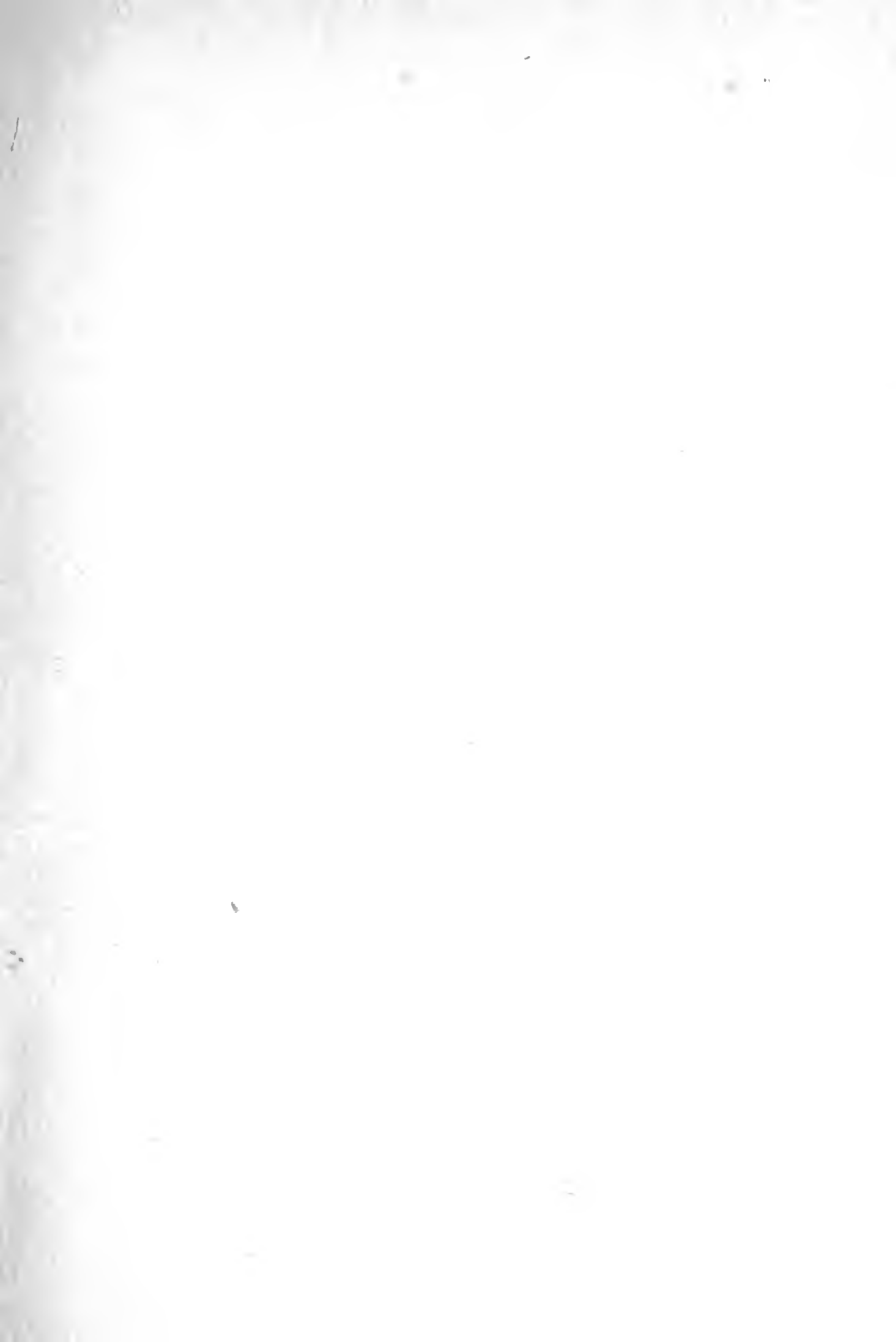
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# HOUSEHOLD CHEMISTRY

FOR THE USE OF

## STUDENTS IN HOUSEHOLD ARTS

BY

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## PREFACE.

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This book is presented for the general study of the subject of chemical operations in the household. It is designed to meet the needs of secondary schools and colleges. For the former purpose, the instructor will find it possible to make such selection of material as will cover the field of work broadly in a semester. A thorough completion of the course indicated in the book would require the attention of the college student for one year. It is highly advisable in this longer course that one third of the period be given to explanation and discussion of the topics in the form of lectures. In the shorter course the object may be accomplished by the more informal conference system.

It has seemed best to include a large amount of descriptive matter in this book, which was not a feature of former editions.

I wish to express my great indebtedness to my assistants, Mrs. Ellen Beers McGowan and Miss Sadie B. Vanderbilt, for valuable assistance and advice in the preparation of this volume.

H. T. V.

May, 1915.

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## CHAPTER I.

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### INTRODUCTORY.

Courses of instruction in Household Economics group themselves principally about foods or other materials used in the household, most of which are of so-called organic origin. Hence some fundamental instruction in the nature of organic compounds is necessary, and preferably should precede a course in household chemistry, which is largely an applied chemistry of the carbon compounds. Often, however, a preliminary course in organic chemistry cannot be introduced into the curriculum. For that reason, an outline of a series of lessons in the chemistry of the carbon compounds is given here, designed to be presented as lectures and experiments running parallel with the work in household chemistry and often merging into it. In such a combined course, the outline as given will need to be adopted to the allowed time, perhaps to the exclusion of the aromatic compounds, and it may be necessary to perform many of the experiments as demonstrations. To give the study its proper emphasis and value, stress should be placed less upon individual than upon type compounds, and upon their inter-relation and properties, always with a view to enriching and making more effective the practical knowledge which the student has of substances met in everyday life.

It may be pointed out, in addition, that a recent course in general chemistry of the most modern type should be

required as a prerequisite of household chemistry. In such a course the subject matter should be so selected that the material handled in household chemistry shall not be entirely unfamiliar. For example, more definite information would be useful with regard to the constitution and properties of the imported metallic elements, and a few of their simple compounds.

### Outline of Course in Organic Chemistry.

#### I. ORIGINAL AND PRESENT MEANING OF TERM "ORGANIC."

Importance of organic chemistry—Some differences between organic and inorganic compounds—Organic chemistry the chemistry of carbon compounds—The carbon atom: its valency; graphic expression of valency; tendency to combine with hydrogen.

#### II. CHAIN HYDROCARBON.

The Methane, Ethylene, and Acetylene Series.

Development of Series—Nomenclature—Common formulae and differential—Properties—Occurrence of important members.

Application to Gaseous and Liquid Fuels.

Experiments: Preparation of Methane, Ethylene and Acetylene.

Reaction for the double bond.

#### III. ISOMERISM APPLIED TO THE HYDROCARBONS.

Nature and effect of isomerism.

#### IV. SATURATION AND UNSATURATION.

Meaning of—General formation of substitution and

addition products—Isomeric forms—Formation of iodoform and chloroform.

Experiment: Preparation of iodoform.

## V. ALCOHOLS.

Derivation from the hydrocarbon through substitution—relation to metallic hydroxides—Nomenclature—General physical and chemical properties and reactions—Source and uses of important alcohols—Isomeric forms: primary, secondary, and tertiary alcohols—Unsaturated alcohols—Glycols and polyhydric alcohols—Sulphur alcohols or mercaptans.

Applications to liquid fuels; to carbohydrates; to fats; to fermentation; preservation of foods.

Experiments: Preparation of ethyl alcohol.

Detection of methyl alcohol.

## VI. ALDEHYDES AND KETONES.

Formation from alcohols—Comparative properties and reactions—Name, source, and uses of important examples.

Application to carbohydrates; preservatives; flavoring extracts.

Experiment: Preparation of formaldehyde, acetaldehyde and acetone.

Reduction by aldehydes, such as the Fehling's reaction.

## VII. FATTY ACIDS.

Formation from aldehydes—Nomenclature—General properties and reactions—Occurrence and properties of

important examples—Unsaturated acids: occurrence and characteristics.

Application to fats and oils.

Experiments: Preparation of acetic acid.

Separation of a fatty acid from a fat.

Illustration of drying and non-drying property.

#### VIII. SCHEMATIC REVIEW OF INTERRELATION.

Hydrocarbon  $\rightleftharpoons$  Substitution  $\rightleftharpoons$  Alcohol  $\rightleftharpoons$   
Aldehyde  $\rightleftharpoons$  Acid

#### IX. ESTERS.

Formation of type esters reviewed—Waxes—Glyceryl esters of fatty acids: general properties; occurrence and properties of important fats and oils.

Application to fats and oils.

Experiments: Decomposition of a fat.

Preparation of ethyl acetate.

#### X. ETHERS.

Formation—Analogy to metallic oxides—Nomenclature—Important example—Properties—Relation of ethers to alcohols; of thio ethers to mercaptans.

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## XII. NITROGEN COMPOUNDS.

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2. *Amines.*

Primary, secondary and tertiary amines—Quaternary ammonium bases—Unsaturated amines and related compounds—Important examples.

3. *Amides.*

Structure and properties—Amides of dicarboxylic acids—Important examples.

4. *Amino Acids.*

Formation—Nomenclature—Properties and reactions—Important examples—Synthesis to peptides—Relation to proteins.

5. *Proteins.*

General composition, properties, etc.

6. *Purin Group.*

Purin ring and substituted purins—Adenin, guanine, hypoxanthin, xanthin and uric acid; caffeine; theobromine.—Pyrimidin base.—Relation to nucleoproteins.

## XIII. AROMATIC COMPOUNDS.

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Coupling diazos and phenols.

Formation of leuco compounds.

Reduction of indigo blue and subsequent oxidation.

Preparation of helianthin and eosin.

## CHAPTER II.

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### ATMOSPHERE AND VENTILATION.

Probably no subject so important to life as the air we breathe is so little understood, nor is there any other instance of so many evils arising from ignorance. A knowledge of the relation of pure air to health and efficiency should be a part of the education of people in general. In no other way will there be a solution of problems of ventilation in homes and public buildings, or of sanitary housing in large cities, and the stamping out of devastating diseases. A fundamental knowledge of the properties and functions of the atmosphere, and the principles of ventilation, is therefore all-important for the student of household chemistry.

**Composition of the Air.**—Pure air is not a compound of definite composition, but a mixture of gases. The two most important, oxygen and nitrogen, occur in the proportion of about 20 parts of the former to 79 of the latter. Other essential constituents are carbon dioxide, which in pure air averages in amount a little over 3 parts in 10,000, or 0.03 per cent. to 0.04 per cent., and aqueous vapor. Traces of argon, krypton, neon, ozone, hydrogen, ammonia, nitrogen acids, nitrites and nitrates, helium, and several other substances are normally found in varying amounts.

In addition to the above, there are always present in ordinary air many substances classed as impurities, the kind and amount varying with the locality. Dust from

the soil and from factory operations is found as suspended matter, together with micro-organisms, pollen, plant seeds, and soot. Offensive gases may contaminate the air of manufacturing centers, but they are usually more disagreeable than dangerous. The air of cities contains anywhere from 100 to 5,000 times the amount of dust and bacteria that is found in country air.

**Properties and Uses of Constituents.**—*Oxygen.*—Oxygen is the life-supporting element for all animals and plants. Diluted as it is with nitrogen, the oxygen of the air is in the condition and proportion best adapted to sustain most forms of life. In materially increased amount it is a poison to human beings; on the other hand, life cannot exist if the proportion falls to four-fifths of the normal, or 16 per cent. instead of about 20 per cent.

In animal organisms, a relatively small amount of oxygen is concerned in the process of respiration. Of 20.9 per cent. inhaled by human beings, 16 per cent. is returned in the exhaled air, together with about 4.4 per cent. of carbon dioxide. The oxygen used, however, in the respiratory exchange suffices to supply heat and energy to the body by means of oxidative processes in the protoplasm of tissue cells.

Plants require oxygen for respiratory and other processes as animals do. Part of the necessary amount is inhaled; part is obtained in the process of photosynthesis, through the action of chlorophyll and sunlight. A plant lacking in chlorophyll, such as a mush-

room, absorbs oxygen directly from the air; green plants, in the presence of sunlight, build up carbohydrate material in their cells by synthesizing carbon dioxide and water, and in the operation release oxygen. The cells use as much of this as they require; the excess is returned to the air. It is estimated that an acre of woodland withdraws in one season about  $4\frac{1}{2}$  tons of carbon dioxide from the atmosphere, and returns  $3\frac{1}{2}$  tons of oxygen.\* In darkness the chlorophyll becomes inactive; the plant then takes oxygen from the air. It is probable that the roots absorb oxygen from the soil and from ground water.

*Ozone*.—Ozone is a peculiar form of oxygen which exists as  $O_3$ . It is produced from  $O_2$  by electrical discharge, by the action of moist air on phosphorus, or by several chemical reactions, such as the action of concentrated sulphuric acid on potassium permanganate. Its odor is noticed around static electrical machines and during thunderstorms. Ozone is a powerful oxidizing agent, but is found only in minute quantities in ordinary air. The salubrity of the air in evergreen forests is ascribed to ozone, formed as a product of the slow oxidation of turpentine and similar plant products.

*Nitrogen*.—Nitrogen is an inert gas; it does not burn nor support combustion, and its chief value to organisms is in the form of compounds. It is not utilized in human respiration except as a diluent of oxygen. In the plant world certain species of bacteria such as the

\* Harrington : *Practical Hygiene*.

micro-organisms found in the root nodules of some legumes, carry nitrogen directly to the pea, bean or clover. How far other plants are able to utilize atmospheric nitrogen is a question. The main source of the organic nitrogen in their tissues is the nitrogen compounds in the soil due to micro-organisms and ammonia and nitrates washed down by the rain.

*Carbon Dioxide.*—Carbon dioxide is a heavy gas which will not support combustion or respiration. It is the result of oxidation processes, either in respiration, fermentation, the burning of tons of fuel, or chemical action in the soil. Harrington estimates that 5,000,000,000 tons are discharged annually into the atmosphere. The amount of carbon dioxide in the air may vary from two parts in 10,000, or 0.02 per cent. in the purest air to 30, 40 or even 100 parts in bad conditions of overcrowding. Only in greater amount, however, such as was found in the Black Hole of Calcutta, is it destructive to animal life. Undiluted, it causes instant suffocation by spasmodically closing the glottis.

On account of the solubility of carbon dioxide in water, considerable amounts are taken out of the atmosphere by rain and go to form carbonates in the soil or remain as carbon dioxide in the water.

*Aqueous Vapor.*—The term aqueous vapor is misleading and does not strictly represent the gaseous form in which the water in question exists in the atmosphere. The amount of aqueous vapor which a given volume of air is capable of holding without condensation depends

upon the temperature of the air. At  $0^{\circ}\text{C.}$ , a cubic meter of air is saturated if it contains 4.87 grams of moisture; at  $20^{\circ}\text{C.}$  or  $68^{\circ}\text{F.}$  it can contain 17.157 grams, and at  $32^{\circ}\text{C.}$  or about  $90^{\circ}\text{F.}$  it may hold 30 grams. It follows that a precipitation of moisture results when the temperature of vapor-laden air changes from a higher to a lower point. The temperature at which moisture is deposited is called the dew point.

The rate of elimination of moisture from bodies depends largely on the amount of moisture already carried by the air. When air is saturated, it can take up no more; evaporation, therefore, cannot occur, and the moisture normally given off by the human body, for example, is deposited on the surface of the skin. This most disagreeable condition of stickiness is associated with days of great humidity in summer, with moist, raw days in winter, and with overheated crowded rooms.

Humidity is measured in terms relative to the saturation point of the atmosphere at any given temperature. A relative humidity of 50 means that the air contains only 50 per cent. of its moisture-carrying capacity at that temperature. The limits of comfort are generally given as between 40 and 75; a humidity of 75 to 100 is oppressive to man but beneficial to plants.

The relation of atmospheric moisture to heat is most important. Water has a great capacity for heat and gives it up slowly. It acts therefore as an equalizer of the sun's heat and a moderator of temperature. In semi-arid and desert regions, where the air is moisture-free,

and at high altitudes where the amount of vapor is relatively less, extreme heat during the day and a sudden fall of temperature at night are observed. It is estimated that the absorptive and radiative power of aqueous vapor is 16,000 times that possessed by air.

*Dust.*—The relation of dust to aqueous vapor is significant. Without this suspended matter in the air there would be little or no precipitation of moisture, but a constant state of saturation would be possible. The particles act as nuclei round which vapor condenses as fog or rain. In large manufacturing cities the prevalence of soot and dust in the air accounts for frequent fogs. Bacteria cling to dust particles and with them are washed out of the air by rain.

**General Properties of the Air.**—*Density.*—The density of the atmosphere varies, the principal factor in variation being altitude. At  $3\frac{1}{2}$  miles elevation it is only one-half as dense as air at sea level and therefore exerts one-half the pressure. The normal pressure of the atmosphere at sea level upon each square inch of surface is about 15 pounds, but this pressure, which amounts to 30,000 pounds on the average body, is not appreciated, since it is exerted equally in all directions. Air pressure is commonly measured by the height of the column of mercury which it is capable of supporting, the recording instrument being called a barometer. A normal pressure at sea level, exerted on the mercury at the base of the barometer tube, is sufficient to raise in the tube a column



of mercury weighing 14.7 pounds. This is called a pressure of 1 atmosphere.

When the mercury falls in the barometer, which usually happens before a storm, it is evident that atmospheric pressure has become less. This is because the air at such times probably contains more than a normal amount of water vapor, which is lighter than air, its density being 9, while air averages 14.5. The term heavy, sometimes used to describe the atmosphere in this connection, is contrary to fact. A further explanation of the barometric condition is found in the fact that as different portions of the earth's surface become unequally heated, the warmer areas impart corresponding heat to their atmosphere. This causes a rising and dilation of air over a given section, the heated column overflowing at the top upon the cooler surrounding atmosphere. Diminished pressure results in the rarefied column, with consequent expansion and a fall in temperature, until the moisture-precipitation point is reached, and the contained vapor of the air is condensed as cloud or rain. In changing from the vapor to the liquid form latent heat is released, which increases the rarefaction, and the upward movement and overflowing of the air column continue. Thus is created a condition of low pressure which the barometer indicates, while in the surrounding areas high barometric readings will be found. The rain area will naturally correspond with the area of low pressure.

*Diffusion.*—By a fortunate provision of nature, gases

of different specific gravities do not lie in strata when mixed, but diffuse until the mass is of uniform composition throughout. If it were otherwise, a layer of carbon dioxide, which is a heavy gas, would blanket the earth, and offensive and poisonous gaseous emanations would make most localities uninhabitable. As it is, all such gases diffuse through the atmosphere as soon as produced. Stratification of the air is not, however, entirely controlled by diffusion. The local movements of air currents caused by unequal heating operate like a motor fan and are a most potent equalizing influence.

*Heat Capacity.*—Air has a considerable capacity for taking up heat, which is utilized in hot air heating.

*Liquid Air.*—Air can be liquefied by causing it to escape slowly from tremendous pressure, so that much heat is absorbed in expansion. The temperature of liquid air is nearly  $400^{\circ}$  below zero Fahrenheit. In this state it volatilizes rapidly at room temperature, the more volatile nitrogen being given off first. This leaves an available source of oxygen, which is utilized in filling oxygen tanks. Liquid air has a faint blue color.

### EXPERIMENTS ON AIR.

1. **Presence of Oxygen.**—Pour an inch of alkaline pyrogallol into a short broad test-tube, close with a rubber stopper, invert and mark the position of the stopper and liquid on a gum label pasted on the outside of the tube, shake the tube well, invert and open under water, mark the level of the water in the tube when open, and explain the phenomenon.

2. **Carbon Dioxide.**—Expose a few drops of lime-water or barium hydroxide on a slide to the air and notice that, by the

end of the lesson, it is cloudy. What is the precipitate? Write the reaction.

3. **Hydrogen Sulphide.**—Moisten a filter-paper with a solution of acetate of lead and expose to the air until the end of the lesson. Notice the black coloration due to the formation of lead sulphide. This test works well in gas-lit rooms.

4. **Aqueous Vapor.**—Saturate a strip of paper with cobalt chloride or iodide, thoroughly dry and expose to the air out and in doors; under moist conditions, it turns pink.

Weigh a small watch-glass containing about 1 gram of fused calcium chloride, wait about 2 hours and weigh again. Note the increase in weight largely due to water.

5. **Dew Point.**—Take the temperature of the room, immerse the thermometer bulb in a glass of water, and add ice little by little until the first indication of moisture is seen on the outside of the glass. If humidity is low, add salt to hasten process. Note the thermometer reading; it is the dew point of the air in the room.

6. **Determination of Relative Humidity.**—Use a sling or whirl psychrometer. This instrument has two thermometers fastened to a frame which can be whirled in the hand. The bulb of one thermometer is covered with muslin which is made wet at the beginning of the test. As the instrument is whirled evaporation around this bulb reduces the recorded temperature until the dew point is about reached, that is, the temperature at which no further elimination of moisture takes place, but condensation occurs. When the wet bulb thermometer registers its lowest point the reading of both is taken and the dew point calculated. (See Glaisher's table. Harrington: *Practical Hygiene*.)

7. **Relation of Dust to Rain.**—Fit a 2-liter flask with a rubber stopper having 2 perforations. Pass 2 pieces of glass tubing through these, long enough to extend nearly half way into the body of the flask. Attach pieces of rubber tubing fitted with pinch-cocks to the free ends of the glass tubing just above the stopper. Put in the flask sufficient water to a little more than

fill the neck when the flask is closed and inverted. Keep the flask inverted and allow the confined air to become saturated with aqueous vapor. Now withdraw some of the air in the flask by suction through one of the rubber tubes. The decreased pressure causes a fall in temperature and a condensation of moisture as haze or fine rain throughout the air space in the flask. At this point introduce air through the rubber tubing to restore the original pressure and the mist disappears. Now wash the air in the flask with the contained water until its dust content is removed. Repeat the experiment and note that no rain is produced in the dust-free air.

**8. Atmospheric Pressure.**—Pour 2 inches of water into a clean ordinary half gallon can, boil vigorously and close the opening with a close fitting cork. Remove the burner and when cool the can will collapse. The can should have a small opening and preferably be rectangular in shape.

### Ventilation.

The scope of this book prevents a detailed discussion of ventilation and ventilatory systems. In fact it does not seem possible at present to make definite statements in regard to standards of temperature and composition of air in a well-ventilated room, since the whole subject of ventilation is undergoing revision. Experts disagree as to the comparative physiological effects of the constituents of vitiated air, and if perfect systems of ventilation have been devised, they are not in general use. However, until all buildings are equipped with such a system as a matter of course, a few facts and principles should be generally known and brought to bear on the ventilation of rooms under individual control.

**Effect of Heat and Humidity.**—It has been well established that the main factors causing discomfort in

poorly ventilated rooms are excessive heat and humidity. With increase in temperature, due perhaps to overcrowding, the moisture in the air increases proportionately toward saturation point. Evaporation from the body now becomes relatively impossible. But at a temperature of 70° F. or over the body depends upon evaporation of perspiration to maintain its heat equilibrium. The danger now arises that the checking of evaporation may cause the cutaneous blood vessels to become so congested that the temperature of the skin is raised and heat transfer by conduction and radiation is increased. This occurs at the expense of the efficiency of the other organs, particularly the brain. Headache, dizziness, and even fever may result. Relief is at once felt in such cases if evaporation is aided by setting in motion the air in the room. If this cannot be done by bringing in free currents of outside air, electric fans answer the purpose.

On the other hand, too rapid evaporation of water from the skin and air passages will cause discomfort. This is felt in the dry air of steam-heated rooms. The skin becomes too dry, the cutaneous nerves are irritated, and the effect is felt by the central nervous system. This trouble may be obviated by the evaporation of water from a dish placed on the radiator.

The relation of heat and humidity to efficiency is clearly pointed out in an article on *Work and Weather*,\* by Dr. Ellsworth Huntington. The efficiency curves of over 500 wage earners in Connecticut were studied dur-

\* *Harper's Monthly Magazine*, Jan. 1915.

ing a period of 4 successive years, and those of 1,600 students at West Point and Annapolis, for periods of 2 and 6 years respectively. The declination in amount of work done is greatest at two periods of the year—through January and a part of February, when windows are kept closed and indoor conditions of temperature and humidity are below standard, and from the latter part of June to the end of August. In the summer of 1911, part of which was the hottest in 100 years in the locality where the observations were made, the efficiency of the operatives dropped astonishingly; in 1913, a cool summer, there was very little lowering of the curve.

**Carbon Dioxide.**—Contrary to former belief, carbon dioxide in the largest quantities likely to occur in the air of a room has little to do with the feeling of discomfort. If the room is kept cool, the increase may be up to 20, 30, or even 40 times the normal amount<sup>1</sup> without appreciable effect, and no serious physiological disturbance results until the carbon dioxide content is raised to about 3 per cent. with a corresponding lowering of the oxygen. This is approximately 75 times the amount present in pure air. At this point Dr. Angus Smith found feebleness of circulation, slowing of heart action, and quickened respiration, but could detect no inconvenience with 2 per cent. Pettenkofer and Voit experienced no discomfort after long exposure to air containing 1 per cent. of carbon dioxide.<sup>2</sup>

<sup>1</sup> Rideal: Report on Hygienic Value of Gas and Electric Lighting, presented before Royal Sanitary Institute, London, 1907.

<sup>2</sup> Education: London, Feb. 1912.

An adult will add 0.6 cubic foot of carbon dioxide to the air in 1 hour. Therefore in a room containing 3,000 cubic feet, the carbon dioxide will increase in that time 0.2 cubic foot per 1,000, or 0.2 part per 10,000, *i. e.*, from an initial amount for pure air of 0.04 per cent., to 0.06 per cent., which is the limit of the standard of purity generally given. Theoretically the air of such a room with one occupant would require renewing each hour, but fortunately the average room, not being airtight, is constantly receiving some outside air through various openings.

**“Crowd Poisoning.”**—Dr. Rideal states that the worst that can be said of even respiratory carbon dioxide is that it is often found in bad company. Emanations of a poisonous nature given off in breathing, cause the unpleasant odors noticeable to a person coming into an occupied room from the outside air. Disease germs are likely to be present, and to circulate more freely if dust is in the air. Moreover, sharp particles of dust may have an irritating or lacerating effect on eyes, nose, or lungs, making the tissues more susceptible to the entrance of bacilli. Tuberculosis is commonly spread in this way.

Experiments made under the direction of C. E. A. Winslow, chairman of the New York State Commission on Ventilation (1914), show the effects of heat, humidity, and stale air. It was found that when the temperature of the room was raised from 68° to 75°, the pulse and blood pressure were affected, and the amount of physical work accomplished fell 15 per cent. None of these bad

effects were felt if the room was kept cool, although the air was allowed to become stagnant for 8 hours, so that the carbon dioxide content increased to about 20 times the amount in pure air. A marked effect of this stale air on the subjects was, however, loss of appetite, although the odors accumulating in the room were not noticed by them. This sub-conscious result was proved by serving standard meals and calculating the amount eaten after a period spent in fresh air and in stale air.

**Methods of Ventilation.**—Of the two methods of ventilation—natural and mechanical—the former is the one which must be depended upon in ordinary houses. Natural ventilation relies upon the movement of air currents caused by differences in temperature and gravity, and the force of wind—an uncertain agent. It takes into account the fact that air becomes lighter when heated, and rises. Heated  $50^{\circ}$  F. above the outside air, the air of a room will be increased one-tenth in bulk, since it expands  $\frac{1}{500}$  of its volume for every degree Fahrenheit. Consequently, since good ventilation requires a constant supply of pure air and a corresponding removal of foul air, there should be an inlet and an outlet, the latter at the top of the room where the heated air can escape, the former nearer the bottom, where the colder air entering can have an opportunity of circulating through the room and pressing the warmer air upward. The problem of ventilation in winter often becomes a question of draughts. If the inlet is arranged so that the air may pass in a vertical direction over the



heads of the occupants of the room, and at the same time be somewhat warmed, this trouble is remedied. If the opened window is the only form of inlet possible, a direct draught can be prevented by placing a frame in the opening covered with some open mesh material such as cheesecloth.

The inlets and outlets should be as far as possible from each other, so that air will not pass directly from one to the other without circulating. An outlet should properly have the motive power of heat or an exhaust, otherwise it may become an inlet for cold air. The wind acts uncertainly as an exhaust at times; a mechanical arrangement is more dependable. A fireplace is a desirable natural outlet, having the extra motive power of heat.

Heating by hot air is favorable to a good scheme of ventilation, provided (1) that a steady supply of pure air from outside is brought in to be heated and circulated through the flues; (2) that an outlet for foul air be provided in the room.

Stoves, steam and hot water heating systems offer little aid to ventilation. On the contrary, stoves withdraw the purer air near the floor for purposes of combustion. Careful attention to ventilation is necessary with these methods of heating.

Too often people live in tight shut rooms in winter because they cannot afford loss of heat by ventilating openings. The injury to health is apparent in even a few weeks, in lessened vitality, susceptibility to colds, and

actual disease. In such cases occasional throwing open of windows with rapid exercise at the time answers the purpose with less loss of heat. If one can become accustomed to free circulation without draughts, the body tone is raised so that less heat is required and the chances of injury on exposure are lessened.

## CHAPTER III.

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### WATER.

Water, or hydrogen monoxide, the universal solvent, was believed to be an element until the experimental work of Cavendish showed it to be the product of the chemical union of hydrogen and oxygen. The proportions in which these gases combine are two parts of H to one of O by volume, and one to eight by weight.

**Physical Properties.**—*Latent Heat.*—Water exists in three states without change of composition: as a gas (steam) at  $100^{\circ}$ ;\* as a liquid (water) between  $0^{\circ}$  and  $100^{\circ}$ , and as a solid (ice) below  $0^{\circ}$ . In passing from the solid to the liquid state, additional energy is required for increased molecular spacing and motion. This is obtained in the form of heat from surrounding objects, and becomes the latent heat of fusion. The amount of heat transformed in this way in melting 1 gram of ice is sufficient to raise the temperature of 1 gram of water from  $0^{\circ}$  to  $80^{\circ}$ , or 80 calories. Conversely, when water freezes, 80 calories per gram are released and appear as sensible heat.

Steam, being a gas, requires more energy for molecular spacing and motion. To change 1 gram of water at  $100^{\circ}$  to steam at  $100^{\circ}$  necessitates approximately 537 (536.6) calories. One gram of steam, therefore, contains 537 calories plus the 100 calories of the boiling

\* Unless otherwise stated, the centigrade scale is used in giving thermometer readings.

water. When steam at  $100^{\circ}$  condenses to water at  $100^{\circ}$  537 calories are given up as heat.

*Specific Heat.*—The capacity of water for heat is so great that it is taken as the standard. The specific heat of water is expressed as 1; that of most other substances in fractions. For instance, the specific heat of aluminium is 0.21, which means that the amount of heat which will raise 1 gram of aluminium  $1^{\circ}$  will raise 1 gram of water  $0.21^{\circ}$ .

*Conductivity.*—Pure water is a poor conductor of heat and electricity, but dissolved matter increases its conductive capacity.

*Boiling and Freezing Points.*—The boiling and freezing points of pure water under standard atmospheric conditions are used as convenient points for standardizing thermometer scales: in the centigrade  $0^{\circ}$ - $100^{\circ}$ ; in the Fahrenheit  $32^{\circ}$ - $212^{\circ}$ ; in the Reaumur  $0^{\circ}$ - $80^{\circ}$ . An increase in atmospheric pressure raises the boiling point, a decrease lowers it. Boiling and freezing points are also affected by substances in solution. Solutions having increased density boil at a higher temperature and freeze at a lower than pure water. If electrolytes are in solution the increase and decrease are greater than in the case of non-electrolytes. For example, the boiling and freezing points of a solution of sodium chloride are higher and lower respectively than those of an equivalent solution of sugar.

*Density.*—The weight of 1 cc. of water at its point of greatest density,  $4^{\circ}$ , is 1 gram. This is taken as the

standard of density, and is used as the unit in specific gravity measurements of liquids and solids. The Baumé hydrometer, an instrument for determining the specific gravity of liquids, floats at the mark O in distilled water at 15.5° or 60° F.

*Compressibility and Expansion.*—Water in the liquid state is practically incompressible. It is calculated that the small compressibility of water causes a lowering of the surface of the ocean to the extent of 600 feet where the depth is 6 miles, or an average depression for the large ocean bodies of 116 feet. On passing toward the solid state, water contracts until it reaches 4°, its point of greatest density. Below this point its volume increases, and at freezing point, 0°, there is a sudden further expansion of 10 per cent. Consequently water at 4° is heavier than at 0°, a provision of nature which makes it impossible for large bodies of water to freeze solid. When water is converted into steam it expands more than most other known liquids. The expression “a cubic inch of water makes a cubic foot of steam” is approximately true.

**Chemical Properties.**—As a chemical agent, water is extremely potent. It acts usually as a solvent, but in many cases produces profound chemical changes. Briefly, the action of water may be classed as follows:

Water of Solution.

Water of Hydration.

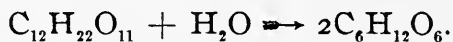
Water of Hydrolysis.

*Water of Solution.*—When any solid dissolves in

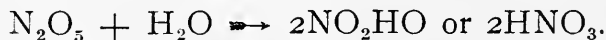
water, loss or gain of heat is apparent, but on evaporating the liquid the solid reappears in the original form. With acids, bases and salts there is electrolytic dissociation in addition to solution.

*Water of Hydration.*—On partial evaporation of the liquid, the soluble substance reappears in changed form, containing a definite amount of the water in the solid state. This is known as water of hydration or crystallization. Familiar examples are washing soda,  $\text{Na}_2\text{CO}_3$ , 10  $\text{H}_2\text{O}$ ; alum,  $\text{K}_2\text{Al}_2(\text{SO}_4)_4$ , 24  $\text{H}_2\text{O}$ ; borax,  $\text{Na}_2\text{B}_4\text{O}_7$ , 10  $\text{H}_2\text{O}$ ; Glauber's salt,  $\text{Na}_2\text{SO}_4$ , 5  $\text{H}_2\text{O}$ , and copper sulphate,  $\text{CuSO}_4$ , 5  $\text{H}_2\text{O}$ .

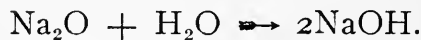
*Water of Hydrolysis.*—Complete hydrolysis is a change in which water enters a substance as H and the hydroxyl OH, splitting it into new compounds generally simpler than the original substance. The changes which food undergoes in the processes of digestion are examples of hydrolysis, such as the breaking down of sucrose into fructose and glucose:



The solution of the non-metallic oxides  $\text{SO}_3$ ,  $\text{N}_2\text{O}_5$  and  $\text{P}_2\text{O}_5$  is another example:



or the solution of caustic alkalies and slaking lime:



*Applications.*—Explain the principle of the ice box, the fireless cooker, the double boiler, the vacuum pan, the digester kettle, the unglazed water jar, the freezing mixture of ice and salt.

Why are cranberry bogs flooded in winter, or tubs of water put in vegetable cellars or under orange trees on frosty nights?

Explain the effectiveness of steam heating, hot water heating, a hot water bag.

Why is salt put on an icy sidewalk in winter?

Why is a scald from a steam burn worse than one from boiling water?

Why does water boil more quickly when there is considerable water vapor in the atmosphere?

How does adding salt to the water in boiling vegetables and keeping the cover on the dish affect the boiling point?

Why is a mixture of ice and salt more effective than ice and sugar in freezing ice cream?

Explain the cooling effect of perspiration.

### EXPERIMENTS ON WATER.

1. **Heat Conductivity.**—Fill an 8-inch test tube two-thirds full of water, grasp the lower end of the tube with the fingers and hold in the flame at a slight inclination from the perpendicular. Note that the upper part will boil before the lower becomes uncomfortably hot to hold. Reverse the order of heating and note the same result. Explain.

2. **Boiling-Point Under Atmospheric Pressure.**—Pour about 250 cc. of distilled water into a half liter round bottom flask supported on a ring stand. Introduce a thermometer so that the

bulb only is immersed in the liquid and apply heat. Note the point to which the mercury rises when the liquid is quietly boiling, raise the thermometer bulb just out of the liquid and take the reading. Is there any difference? Does the thermometer indicate any higher degree of heat when the liquid boils violently?

3. **Boiling-Point Under Reduced Pressure.**—Select a cork which fits the flask tightly, pierce a hole through it and insert a thermometer. Now half fill the flask with water and boil the liquid. When in active ebullition, close the flask with the cork and thermometer and instantly withdraw the heat. When the liquid ceases to boil, read the thermometer, and grasping the neck of the flask with several folds of a towel, hold it under running cold water. What happens? Read the thermometer and explain.

4. **Influence of Soluble Matter.**—Note the boiling point of a solution of 10 grams of salt in 100 cc. of distilled water. Observing the same conditions throughout, repeat the experiment, using sugar. How do the boiling points compare? Explain. Cool each solution to  $15^{\circ}$  and take its specific gravity.

5. Take the specific gravity of a mixture of equal volumes of water and 95 per cent. alcohol, and note its boiling point. Explain.

6. Weigh out 30 grams of table salt, measure 100 cc. of distilled water, and use only as much of the water as is required to make a saturated salt solution (pickle). What is the required proportion of salt to water? Take the specific gravity of the solution and its boiling point, and compare with Experiment 4. Will a fresh egg float or sink in this liquid? Evaporate a few drops of the solution on a microscope slide and observe the salt crystals under a low power lens.

7. **Hydration and Hydrolysis.**—Take a tablespoonful of common plaster, mix this with half the volume of water in a porcelain dish, stirring with a thermometer. Record the result and explain.

8. Slowly pour about 10 cc. of strong sulphuric acid into 50 cc.



of cold water, stir well with a thermometer, and from time to time record the temperature. Explain.

9. Using a burette, carefully mix exactly 52 volumes of alcohol (95 per cent.) and 48 volumes of water in a 100 cc. stoppered cylinder. How many volumes result? Explain.

10. Add half a teaspoonful of dry pulverized lime ( $\text{CaO}$ ) to an equal volume of cold water, stir the mixture with a thermometer, adding more water if necessary, and record the thermometer reading. Explain and write reaction.

Water may be made to show the path of travel of convection currents as follows:

Fill a 500 cc. beaker two-thirds full of distilled water, place over wire gauze on a ring stand and apply heat by placing the Bunsen burner on one side of the bottom. When the water is warm drop into it a few crystals of fuchsin or other soluble coloring matter and watch the path of the crystals through the water.

### Potable or Drinking Water.

**Classification of Natural Waters.**—Natural waters are never pure, as they dissolve or hold in suspension gases, liquids, and solids with which they come in contact. The following is a convenient classification:

Natural Waters	Atmospheric	Rain	—Contains very little dissolved solids but dust and gases of the atmosphere.
		Snow	
		Fog	
	Terrestrial	Sweet	Surface—Cloudy, usually a large amount of suspended matter, minimum of dissolved.
			Underground—Clear, minimum of suspended matter, maximum of dissolved.
		Salt	Brines—over 5% soluble salts. Sea water—3.6% solids. Mineral—excess of unusual mineral matter and gases.

Potable or drinking water should be clear, free from odor and color, and should contain not more than 20 grains of solids per U. S. gallon, of which not more than one-half is organic matter.

The soluble mineral matter in water consists of a mixture of the following salts:

Carbonates	}	of	{	Sodium
Bicarbonates				Potassium
Sulphates				Calcium
Chlorides				Magnesium

together with oxide of iron and silica in minute amounts. An excess of chlorides may be due to sewage or animal contamination, excess of lime causes hardness, and excess of iron usually is apparent from the color and is probably due to the solvent effect of organic matter in the water.

On boiling, water loses its dissolved gases, hence distilled or sterilized water is flat or stale.

**Qualitative Examination of Water.**—The importance of guarding a water supply from contamination is evident. Equally important are frequent expert analyses of the supply in order to be sure that the safeguards used are effective. No attempt will be made in this work to give methods for the quantitative estimation of the impurities found in water. However, certain qualitative tests may be given which will aid in detecting such impurities when present in abnormal amounts; it is only when found in such amounts that the water is open to suspicion. The impurities are for the most part harmless in themselves, but if found demand quantitative analysis and

possibly bacteriological examination. A thorough investigation of the surroundings and of the sources of contamination of the supply, and great care in taking the sample, are essential in making an examination of any water.

The tests usually made are with regard to color and appearance, odor and taste, and for the presence of total solids, free and albuminoid ammonia, nitrogen as nitrites and nitrates, chlorine, temporary and permanent hardness, and sometimes phosphates, sulphates, etc.

The color and turbidity, odor and taste of a drinking water are not in themselves indications of its purity, but taken with other data, help in forming an opinion of the sample. A clear, colorless, tasteless water may be polluted; on the other hand a safe water may have acquired color from dissolved iron, or a "peaty" taste from swamp vegetation, or a fishy odor from the decay of algae.

*Odor.*—Rinse a stoppered flask with the water to be tested, fill it two-thirds full of the sample, cork, shake violently, remove the stopper and note the character and intensity of the odor. Replace the cork, warm the water over a water bath to 40°, remove, again shake thoroughly observe the odor as before. The odor will be strengthened by heating. A putrid or offensive smell probably indicates sewage contamination.

*Color and Turbidity.*—Fill one of two Nessler's tubes with the water under test, the other with an equal volume of distilled water. Compare the color and clearness of the two by observing against white paper.

*Total Solids.*—This is a method of determining the total residue left by the water on evaporation, and the proportion of mineral and organic matter present. The

following experiment gives an approximate estimation<sup>1</sup> of total solids:

1. Weigh a clean porcelain dish, measure into it 100 cc.<sup>2</sup> of the water to be tested, and evaporate to dryness over a water bath. Cool and weigh. The increase in weight gives total solids. Apply gentle heat and notice any charring (due to organic matter). A sour odor at this point indicates sewage contamination; a peaty odor, the presence of swamp water. Continue heating until the residue is white or nearly so; cool and weigh. The loss in weight represents organic matter, the residue is mineral matter. Some inaccuracy must be expected, due to the action of heat in volatilizing carbonates and alkali chlorides.

2. Concentrate 100 cc. of the water to about 10 cc., cool and test for mineral matter as follows:

(a) Phosphates. A few drops of the liquid, acidified with  $\text{HNO}_3$ , is added to a larger quantity of ammonium molybdate and heated in boiling water. A yellow crystalline precipitate indicates phosphates. Phosphates are seldom found in drinking water. If present they indicate probable sewage contamination.

(b) Chlorides. Add a drop of  $\text{HNO}_3$ , then  $\text{AgNO}_3$ . A white precipitate of silver chloride soluble in  $\text{NH}_4\text{OH}$ , indicates chlorides.

(c) Carbonates. To 40 or 50 cc. of clear lime water add a small amount of the water to be tested. Any cloudiness soluble in acetic acid shows carbonates. Make the flame test. A yellow color indicates sodium; a violet, potassium. View the latter through blue glass.

(d) Iron as ferric compounds. Slightly acidify with  $\text{HCl}$  and add  $\text{NH}_4\text{SCN}$ . A blood red color indicates iron. Or, to

<sup>1</sup> For exact methods, see *Air, Water and Food*, Richards and Woodman, and *Examination of Water for Sanitary and Technical Purposes*, Leffmann and Beam.

<sup>2</sup> If 100 cc. are evaporated, the residue in milligrams represents so many parts per 100,000; if 58 cc. are taken, each milligram of residue is equivalent to a grain per U. S. gallon.

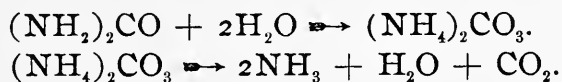
determine the oxidation of the iron, to the acidified water add  $K_4Fe(CN)_6$ . A dark blue color indicates ferric salts. With  $K_3Fe(CN)_6$  a blue color indicates ferrous compounds.

(e) Calcium. Add  $NH_4Cl$ ,  $NH_4OH$ , and  $(NH_4)_2C_2O_4$ . A white crystalline precipitate of calcium oxalate forms on boiling. If calcium is present, filter, and save the filtrate for (f).

(f) Magnesium. To the above cooled filtrate add sodium phosphate. Magnesium shows as a white crystalline precipitate of ammonium magnesium phosphate.

(g) Aluminium. Add  $NH_4Cl$  and an excess of  $NH_4OH$ . Warm the solution. A white flocculent precipitate of aluminium hydroxide appears on standing, if considerable alum is present. The logwood test (p. 174) is more delicate for small amounts.

*Free and Albuminoid Ammonia.*—Two forms of ammonia are looked for in water—free and albuminoid. Neither of these is injurious in itself, but their significance lies in the fact that they indicate conditions favorable for pathogenic bacteria. The free or ureal ammonia, if present in any quantity, is considered to show recent sewage pollution as, although it is found in rain water, and may be formed by the decay of certain algae, it is directly associated with animal excretions, *e.g.*, urea. Urea readily yields free ammonia as follows:



Since ammonium carbonate decomposes as above on heating, it is evident that free ammonia can be obtained by simply boiling the water.

Albuminoid ammonia will not volatilize by this treatment. When present, it indicates undecomposed organic

nitrogen, generally as low forms of plant life. It is necessary to oxidize these substances to volatile compounds before this form of ammonia can be obtained by distillation.

*Determination of Free and Albuminoid Ammonia.*—The method to be followed is distillation, successive distillates to be obtained and tested with Nessler's solution, which gives a yellow or brown color in the presence of ammonia.

*Directions.*—Thoroughly cleanse and rinse with distilled water a round bottom half liter flask and a number of 6-inch test tubes. Connect the flask with either a condenser or a long piece of glass tubing arranged to deliver into the receiving test tubes, which in this case must be cooled by running water or ice. Make all connections tight. Fill the flask about two-thirds full of the water to be tested and distil with moderate heat. Collect distillates in equal amounts in successive test tubes, about 25 cc. in each, and add to each the same number of drops of Nessler's solution. Observe any deepening of color by looking down through the tube against a white background. The color may be compared with standard ammonia solutions. Continue the distillation until a sample shows no added color with Nessler's. Save the distillates for comparison with the yield of albuminoid ammonia in the following:

To the balance of the water in the flask add alkaline potassium permanganate in the proportion of about 15 cc. to 200 cc. of water. Distil with steady moderate heat, collect and test successive distillates as before. The alkaline permanganate solution oxidizes the nitrogen in the form of albuminoid ammonia to compounds yielding free ammonia.

*Nitrites and Nitrates.*—The presence of nitrites in water is supposed to be due either to the incomplete nitrification of ammonia or to the reduction by micro-

organisms of nitrates already formed. While traces of both may occur in all natural waters, a large quantity suggests previous pollution by nitrogenous organic matter of animal origin. This material begins the nitrogen cycle; by decomposition and the work of micro-organisms ammonia compounds follow, and these in turn are oxidized by aërobic organisms to nitrites. Further oxidation by another group of organisms converts these into nitrates. If now nitrates come within reach of chlorophyll bearing plants, they complete the cycle by converting the oxidized nitrogen back to organic nitrogen again. The importance of nitrite and nitrate determination in studying a water supply is evident.

In one of three Nessler tubes put 100 cc. of nitrite-free water (use distilled), in another the same amount of the water under test, in the third nitrite water (to be furnished by the instructor). To each add 5 cc. of freshly prepared mixture of equal parts of sulphanilic acid dissolved in acetic acid, and naphthylamine acetate dissolved in dilute acetic acid. Mix and allow to stand 30 minutes. If the solution becomes pink the water contains nitrites.

*Chlorides.*—Chlorine is found mostly as sodium chloride, although other chlorides may be present. The amount of sodium chloride in any given water supply is affected by the character of the soil, proximity to the ocean, etc., but it should be constant for the locality. Any marked increase over the normal figure indicates sewage contamination.

Place in a small casserole or porcelain dish about 100 cc. of the water to be tested, and in another dish the same amount of distilled water. Add to each 2 or 3 drops of potassium chromate

solution, then add drop by drop a dilute solution of silver nitrate (N/10) stirring after each drop until a faint tinge of red remains. Obtain the same tint in each, and note the number of drops of silver nitrate used in each case. Each drop of silver nitrate solution is equivalent to 0.000293 gram sodium chloride.

*Oxygen Consuming Power.*—This is a method of estimating the organic matter in water by its decolorizing power in the presence of potassium permanganate. The test is not especially significant even when performed quantitatively, as it is not delicate or definite.

Fill two clean 8-in. test-tubes, one with the water to be tested, the other with distilled water, and add to each the same amount of acidified potassium permanganate solution. Be careful not to obtain too deep a shade and see that the shades match. On standing 10 minutes, there should be an appreciable lightening in color, greatest in the tube of water under test. If the color entirely disappears, the amount of organic matter is probably dangerously great. Compare with the test under total solids.

Ice used in drinking water should be examined as to purity. A sample should be melted and tested by the method described for water.

### Water Purification.

**Household Methods.\***—*Boiling.*—Boiling is the simplest and most effective household method of making a drinking water safe, as typhoid and other pathogenic bacteria are killed. Boiled water has a flat taste due to the loss of dissolved gases, but this can be remedied by aeration.

*Effect of Charcoal.*—Charcoal is useful as a decolorizer and deodorizer.

\* For public methods of water purification, see *Food Industries*, Vulté and Vanderbilt, and *Our Water Supply*, Mason.



To 50 cc. of water add enough vinegar to give it a distinct but not deep yellow color then divide into two equal parts. Filter one through dry freshly ignited boneblack several times and compare the color of the resulting liquid with the original solution.

*Effect of Alum.*—Alum readily ionizes in water, forming a flocculent precipitate of aluminium hydroxide, which collects any suspended matter and removes it by sedimentation. It is thus useful in clearing turbid water for laundry purposes, swimming pools, etc., and is used on a large scale in some filtration beds.

Take any sample of cloudy or slightly colored water, even soapy water will answer. Add a very small quantity of finely powdered alum, shake well, filter, and compare with the original sample. Write the reaction for the formation of aluminium hydroxide.

Water should be neutral or slightly alkaline to work well with alum.

*Filtration.*—Prove by the following experiment the effect ordinary filtration has upon substances in solution or suspension in drinking water:

Filter a dilute salt solution; taste the liquid. Is any change produced? Add to the filtrate a few drops of  $\text{AgNO}_3$ , shake well and filter again. Note any difference.

Household filters of the Berkefeld, Pasteur-Chamberland and Aqua Pura types are effective, as they remove micro-organisms as well as suspended matter.

*Distillation.*—This is an effective method of purifying water, but not so simple for household practice as boiling. From the following experiment the student is expected to determine the effect of distillation with reference to volatile and non-volatile substances:

Using the same apparatus as for the determination of ammonia, distil with moderate heat a solution of about 2 grams of copper sulphate in 250 cc. of water. Is this solution acid? Carefully examine the distillate for copper sulphate. Remove the burner, cool the apparatus, and add 5 cc. of ammonia, shaking well; a deep blue color should be obtained. Distil this liquid and test the distillate as before. Explain.

### Hard and Soft Water.

With reference to its detergent action, two kinds of water are recognized—hard and soft. Hard waters contain calcium and magnesium salts which are undesirable in many industries. They produce the troublesome boiler scale, they are a serious objection in sugar refining, and in many textile operations, especially in dyeing. In the household hard water makes a poor detergent, because soluble calcium and magnesium salts form insoluble compounds with soap, which not only have no cleansing value, but produce a troublesome curd. A certain amount of soap must be lost in this way before a lather will form and cleansing begin. The degree of hardness a water possesses may be measured by its soap-destroying power. The total hardness of most water is of two kinds—temporary and permanent.

**Temporary Hardness.**—This form is caused by carbonates of calcium and magnesium held in solution as bicarbonates by carbon dioxide present in the water. Boiling expels the  $\text{CO}_2$ , causing a precipitation of calcium and magnesium carbonates, and the temporary hardness is removed. Calcium hydroxide is often used on a large scale for the same purpose. Its effect can be shown as follows:

Pass a current of  $\text{CO}_2$  gas into a small amount of lime water until the precipitate clears. What was the precipitate? What does the water now contain? Write the reactions. What happens if more lime water is added? Write the reaction, and show that for every nine parts of hardness four parts of  $\text{Ca}(\text{OH})_2$  are required.

**Permanent Hardness.**—Permanent hardness is due to the presence of calcium sulphate and other soluble salts of calcium and magnesium, not carbonates, held in solution by the solvent action of the water itself. Such a water cannot be affected by boiling, but may be softened as follows:

1. Prepare a hard water by dissolving 0.1 gram of calcium sulphate in 500 cc. of distilled water. Add sodium carbonate solution to a portion, and note the result. Write the reaction. Filter and save the filtrate.

2. Roughly determine the amount of soap solution necessary to make a lather lasting 5 minutes in (a) 100 cc. of the above filtrate, and (b) an equal amount of the untreated hard water. What is the effect of the  $\text{Na}_2\text{CO}_3$ ?

**Quantitative Estimation.**—To estimate the total hardness of a given water the procedure may be as follows:

Make a standard soap solution by dissolving 10 grams of good castile soap in sufficient 90 per cent. ethyl alcohol to make up to 1 liter. For use mix 100 cc. of this soap solution with 100 cc. of distilled water and 30 cc. of 95 per cent. alcohol.

Put 58 cc. of the water under test in a clean stoppered 8-ounce bottle, add the soap solution  $\frac{1}{2}$  cc. at a time, shaking thoroughly after each addition. Continue until a lather is formed which will cover the surface of the liquid when the bottle is placed on its side, and will last 5 minutes. Note the amount of soap solution used.

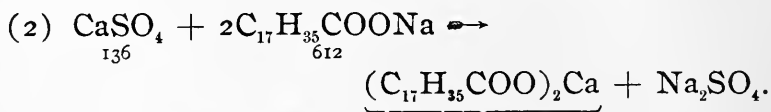
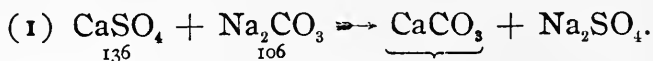
Estimate the total hardness of the water in grains per gallon by using the following data:

One U. S. gallon contains 58,318 grains, 58 cc. contains 58,000 milligrams. Therefore, 58 cc. represents a miniature U. S. gallon, and 1 milligram per 58 cc. stands for 1 grain per gallon, approximately. One cc. of the standard soap solution is the equivalent of 1 milligram of Ca, calculated as  $\text{CaCO}_3$ .

For example, if 10 cc. of soap solution are used, a gallon of the sample contains 10 grains of Ca, spoken of as 10° of hardness. This will be the total hardness of the water.

To estimate the temporary hardness, boil 58 cc. of the sample for 1 or 2 minutes, cool to the temperature of the unboiled water, and make up with distilled water the loss by evaporation. Add the soap solution as before and note the amount required, now that the temporary hardness has been removed. In this case the permanent hardness has been overcome by the soap solution, and the difference in the amounts of the soap solution used in the two cases is the measure of the temporary hardness of the water.

*Use of Washing Soda.*—Washing soda is cheaper and more efficient than soap in softening hard water. The following equations show the ratio of efficiency between the two:



Therefore 612 pounds of pure soap are required to do

the work which 106 pounds of washing soda will do, making a ratio of 6 : 1. But since much yellow laundry soap is only about one third actual soap, the balance being resin, water, and other substances, the ratio becomes 18 : 1, and in actual practice 1 pound of washing soda is considered equivalent to 18 or 20 pounds of soap. A white laundry soap of good quality averages about 75 to 85 per cent. actual soap.

*Problem.*—A water contains 15 grains (approximately 1 gram of Ca per gallon. How much of  $\text{Na}_2\text{CO}_3$ , white soap, and yellow laundry soap will be required to overcome the total hardness of 500 gallons? Assume that the 15 grains of calcium are in the form of calcium sulphate.

For exact methods of hardness determination, see *Hehner's alkalimetric method*.

Natural soft waters are usually recommended for the laundry, solely because they are lacking in soluble lime and magnesia compounds which would waste soap. But organic matter present in this class of water, through stagnation or from soil rich in humus, dissolves notable quantities of metallic oxides from containers and conduits, so that water of this class may become hard from the presence of soluble organic salts of such elements as iron, lead, copper, tin, zinc, etc. In the usual hot water supply of the household this is noticeably the case. So that a moderately hard water—temporary hardness best for the cold supply—which will deposit insoluble lime compounds on the exposed metallic surfaces, is a safe-

guard. Probably the ferrous compounds of iron are the worst to deal with, as they usually are not noticeable from lack of strong color, but readily show in the oxidized form as iron rust spots after drying and ironing white garments. If iron is present it should be completely removed, either by long boiling and settling or filtering, or by adding washing soda, borax, or ammonia, then boiling and settling. Organic matter may be disclosed by the permanganate test. If present in considerable quantity it would be well to oxidize both the ferrous compounds and the organic matter by means of additional permanganate and heat, finally settling or filtering, to remove any residue.

## CHAPTER IV.

### METALS.

The aim of this chapter is the study of the physical and chemical properties of metals, rather than of their compounds, especially with regard to their use in the household. Therefore only those in common use will be considered. Such metals are iron in its various forms, nickel, zinc, copper, aluminium, silver, lead, tin and certain alloys.

Iron, (Ferrum) Fe, occurs in nature largely in the form of oxides: hæmatite,  $\text{Fe}_2\text{O}_3$  (red), and magnetite,  $\text{Fe}_3\text{O}_4$  (black), the latter possessing magnetic qualities and commonly called lodestone.

The metal is obtained by fusing the ore in shaft furnaces with excess of carbon and enough limestone to furnish a fusible ash or slag with the silicious matter present in the ore. The following equations explain the reduction and slagging:



The product, "pig iron," or crude cast iron, contains from 3-4 per cent. of carbon as graphite and combined carbon or carbide of iron,  $\text{Fe}_3\text{C}$ , rendering the mass fusible. By careful smelting in small shaft furnaces called "cupolas," the pig iron is obtained in the form of gray, white and mottled iron, depending on the rapidity of cooling the moulds. Pig iron frequently contains small amounts of impurities, sulphur and phosphorus,

rendering the product short or brittle, while hot or cold; during the refining process these are almost entirely removed in the slag.

Cast iron is brittle and hard, it melts without softening at  $1,200^{\circ}$  and yields a thin liquid which may be cast in sand moulds. The quality of the product depends largely on the purity of the iron (freedom from S. and P.), its temperature of cooling, and the smoothness of the mould.

Cast iron heats more slowly but retains its heat better than other forms of the metal, hence its use for oven plates, sad-irons, stove lids, etc. If heated repeatedly to redness in presence of air and quickly cooled its carbide content increases at the expense of the graphite, and it becomes whiter and more brittle. This causes the frequent cracking of old stove lids. Slow cooling allows less carbide to form; as a result the lid is less brittle, less liable to crack, and has a darker appearance. On the other hand, the hardness of carbide is desirable in sad-irons, accordingly they are frequently heated to a high temperature and plunged into cold water. Cast iron can be made harder than steel, and is sometimes used for the wheel in glass cutters. It does not oxidize as readily as steel or wrought iron.

Malleable iron is intermediate between cast and wrought iron. It is made by slowly cooling cast iron to increase its graphite content and elasticity. It is therefore softer and less brittle than ordinary cast iron, and is much used in house hardware.



Wrought iron and steel are prepared from pig iron by burning out part of the carbon in hot air furnaces of special construction. The reverberatory furnace for producing wrought iron is really a large oven heated by gas and provided with a powerful blast of hot air. Liquid pig iron is run on to the hot furnace bed where the excess of oxygen removes the carbon as follows:  $C_2 + O_2 \rightleftharpoons 2CO$ . As the CO escapes from the liquid mass it produces a bubbling like any boiling liquid. Gradually as the carbon is burned out, the iron becomes pasty or semi-solid and is collected in balls with large pokers operated by hand (puddling). When the balls are of sufficient size they are removed with tongs, squeezed to remove slag and rolled into short bars (blooms or billets). The blooms are then reheated until soft and rolled in bars and rods; when cold the bars may be drawn down through steel dies into wire of almost any degree of fineness. They are cold forged into nails and tacks. Piano wire, the purest form of iron, contains 99.7 per cent. Fe, the balance is mainly carbon. Cold wrought iron is quite soft, bends easily and has great tensile strength. It does not melt readily ( $1,600^\circ$ ) but softens on heating and may be forged and welded.

Steel is a form of iron between cast and wrought, containing 1.5 per cent. carbon. When heated and slowly cooled it is soft (mild), but if suddenly cooled is harder than glass. Hardened steel cautiously reheated, may be softened to any desired extent (tempering). At a high temperature steel melts and may be cast like iron.

Two kinds of steel are manufactured, *i. e.*, Bessemer, the cheaper variety used for rails, plate for making so-called sheet tin and galvanized iron, wire nails, etc., and open hearth steel, a more expensive variety used for cutlery and tools.

*Bessemer Process.*—The cast iron is first melted in a cupola, and then run into a special furnace (the converter), where a powerful blast of hot air bubbles through the molten liquid and quickly (15 minutes) burns out the carbon and other impurities and even produces some oxide. Just at this point, a small portion of molten cast iron containing manganese and the proper amount of carbon is added and the mixture immediately poured into the moulds and cooled. The function of the manganese is to assist in holding the carbon in solution.

*Open Hearth Method.*—The cast iron is melted in a gas furnace with dish-shaped bed together with scrap wrought iron and iron ore. After 8 or 10 hours heating, the operation is complete and the liquid steel is drawn off and cast in ingots.

Steel rusts much more readily than cast iron and usually needs, especially if polished, a protecting coat of oil. Rust may be removed from iron or steel by soaking in kerosene and rubbing with fine emery or carborundum and oil, but stoves and sad-irons should not be coated with kerosene and allowed to stand, as unsaturated compounds in the hydrocarbon take up oxygen and cause the iron to rust.

**Galvanized Iron.**—See zinc.

**Properties of Iron.**—Iron has a specific gravity of 7.8, and when pure fuses at about  $1800^{\circ}$ . It is strongly attracted by magnets. In moist air it oxidizes readily, forming red oxide or common iron rust,  $\text{Fe}_2\text{O}_3$ . This oxide is soft and friable and does not protect the metal from further action. It is slightly soluble in water, giving it a characteristic taste, experienced in drinking water conducted by iron pipes. The other type of oxide,  $\text{Fe}_3\text{O}_4$ , is formed by the oxidation of hot iron, or by the action of superheated steam and carbon monoxide (Barff Process).  $\text{Fe}_3\text{O}_4$  forms a dark gray adherent but brittle coat and protects the metal from further action. It is called the magnetic oxide or blacksmith's scale. Russia iron is sheet iron which has been given this lustrous protective oxide coat. It is used for stovepipes, etc. The red oxide forms the basis of pigments such as Venetian and Tuscan red.

Iron reacts readily with warm dilute acids, but resists the action of alkalies.

#### EXPERIMENT.

Boil small pieces of bright and rusty iron in separate test tubes in the following liquids: Dilute hydrochloric acid (1:1); 20 per cent. acetic acid, and 10 per cent. caustic soda solution. Note comparative strength of action. Filter off the liquid in each case, and test with ammonium thiocyanate in the presence of hydrochloric acid. A blood red color shows iron in solution. Record the results. Write reaction between  $\text{Fe}_2\text{Cl}_6$  and  $\text{NH}_4\text{SCN}$ .

**Nickel**, a hard white metal, occurs in the pure state only in meteorites, but is found combined in several minerals. It is obtained by smelting in the blast fur-

nace. As it takes a high polish and is only slightly susceptible to oxidation in moist air, it is largely used as a protective and decorative coating for iron and copper. The method of plating nickel on iron is similar to silver plating. The bath contains ammoniacal nickel sulphate,  $(\text{NH}_4)_2\text{SO}_4, \text{NiSO}_4, 6\text{H}_2\text{O}$ , in which the article to be plated is suspended, after having been cleaned by acid. This forms the cathode, and a nickel plate the anode.

Nickel plated articles should always be cleaned with a mixture of diluted ammonia and whiting, or rouge, and polished with soft cotton waste.

Nickel has a specific gravity of 8.8, and a melting point of  $1500^\circ$ - $1600^\circ$ . As an ingredient of alloys, nickel is found in German silver (nickel 1 part, zinc 1 part, copper 2 parts), and in coin nickel (copper 3 parts, nickel 1).

It is not active with dilute acids, and like iron resists the action of alkalies.

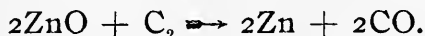
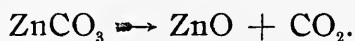
#### EXPERIMENT.

Heat small pieces of pure nickel with dilute acids and alkalies as under iron and record the results. Soluble salts of nickel have a green color and yield a black precipitate,  $\text{NiS}$ , with ammonium sulphide. Neutralize acid solutions with  $\text{NH}_4\text{OH}$  before adding  $(\text{NH}_4)_2\text{S}$ . Write reaction between  $\text{NiCl}_2$  and  $(\text{NH}_4)_2\text{S}$ .

Pure nickel utensils are valuable in the household, but the initial cost is comparatively high. In the laboratory they form a desirable substitute for iron.

**Zinc** occurs chiefly as calamine or zinc blende,  $\text{ZnCO}_3$ . After calcination to drive off  $\text{CO}_2$ , the oxide is mixed

with carbon and distilled in earthen retorts at 1,300-1,400°; crude metallic zinc "spelter" condenses in the receivers and CO burns at a small opening.



Zinc is bluish white, highly crystalline and brittle when cold. By heating to 120-150° and rolling under hot rolls it remains pliable and soft on cooling (sheet zinc). At 200-300° it becomes brittle again, melts at 433° and boils at 920°. Its specific gravity is 7.

Zinc burns in the air with a bluish white flame, yielding a white oxide which is the base of the pigment Chinese white. Zinc oxide is a common ingredient of face creams and other toilet preparations.

In moist air, it oxidizes and absorbs CO<sub>2</sub>, forming a thin adherent coat of basic carbonate which protects the metal from further change. Dilute acids readily dissolve this coating and thus restore the original brilliancy. Acids and alkalies freely attack zinc, liberating hydrogen and producing soluble compounds which are poisonous, hence zinc vessels should never be used for the preparation or storage of food. Do not attempt to cleanse zinc or galvanized iron with anything but neutral soap and hot water.

Sheet zinc is frequently used for roofs, gutters, cornices and leaders of buildings; but does not last well near the seashore, on account of the salt in the atmosphere.

The molten metal mixes in all proportions with copper, tin and antimony. See German silver, brass, etc.

Zinc, both cast and rolled, is largely used in primary batteries. It lasts much better if cleaned with dilute sulphuric acid and coated with mercury (amalgamated).

#### EXPERIMENT.

In a dilute salt solution immerse bright strips of sheet copper and zinc in metallic contact. Prove by examination of the liquid which element suffers by the action. If zinc is in the solution, potassium ferrocyanide will give a white flocculent precipitate of zinc ferrocyanide in acid solution. Test for copper by adding an excess of ammonium hydroxide; a blue color shows its presence.

**Galvanized iron** is sheet iron or steel which after being cleaned with acid is dipped in molten zinc. It is practically a zinc article, resists rust, and should not be used as a receptacle for food.

**Copper.**—Copper (cuprum,<sup>1</sup>) Cu, is found native, also as sulphide and carbonate. Native copper ore is crushed, washed to remove rock and melted with flux. The metal usually contains a small amount of silver which is removed by electrolysis. Carbonates and oxides are fused with coal to reduce the metal. Sulphide ores containing iron require complex treatment; in Montana the procedure is as follows: Partial oxidation by roasting, and subsequent fusion in Bessemer converter (with silicious lining) during which sand and air are blown through the molten mass. The iron is oxidized and combines with

<sup>1</sup> The term "Cuprum" was derived from the island of Cyprus in the Mediterranean, where copper was first mined and extracted.

silica forming a slag, which floats on the copper. Sulphur, arsenic and lead are oxidized and volatilized.

Copper is refined by electrolysis in the following manner: Thin copper sheets coated with graphite are suspended in tanks of copper sulphate solution and connected with negative pole of the dynamo; opposite are heavy plates of crude copper connected with the positive pole. Pure copper is deposited on the cathode, while the  $\text{SO}_4$  ionizes the anode. The impurities not ionized fall to the bottom of the tank.

**Properties.**—Copper is a red metal melting at  $1,057^\circ$ . It is a good conductor of heat and electricity, is very malleable and ductile, and has a specific gravity of 8.9. Several oxides of copper are known; two important ones are the black or cupric oxide,  $\text{CuO}$ , and the red or cuprous oxide,  $\text{Cu}_2\text{O}$ . The latter forms slowly in dry air; in moist air green basic carbonate (not verdigris) is formed. Copper utensils are often lined with tin to prevent the formation of this coating. When free from oxide copper resists the action of alkalies, organic acids and most mineral acids, and is much in demand for the manufacture of apparatus used in food preparation, *e.g.*, vacuum pan for sugar, milk, etc., apparatus for canning and preserving, candy making and beer brewing. Large hotels and restaurants use copper cooking utensils.

The most important alloys of copper are:

Brass, containing .....	18-40% Zn,
Bronze, containing .....	11% Zn, 3-8% Sn, some Pb,
Gun metal, containing.....	10% Sn,
Bell metal, containing .....	25% Sn,
German silver, containing. ....	19-44% Zn, 6-22% Ni.

Brass is essentially like copper in its properties.

Metallic copper and its alloys are readily cleaned with dilute oxalic acid or ammonia. In the laboratory tarnished copper may be cleaned as follows:

#### EXPERIMENTS.

1. Heat a piece of tarnished copper wire in the upper part of the Bunsen flame. Note the change from cuprous to cupric oxide. When the wire glows drop it immediately into a test tube of methyl alcohol. What is the odor observed? Note the appearance of the copper. Complete the reaction:  $\text{CH}_3\text{OH} + \text{CuO} \rightleftharpoons$

2. Heat small pieces of clean and tarnished copper in the reagents described in experiment 1, p. 47. Finally pour off the liquids and add to each an excess of ammonia; a blue color shows the presence of copper. Have the pieces of copper been visibly affected? Write the reaction between  $\text{CuCl}_2$  and  $\text{NH}_4\text{OH}$ .

3. Compare the heat conductivity of copper and iron by holding the ends of copper and iron wires of equal length and size in the Bunsen flame.

**Aluminium**, often called aluminum, is the most abundant of the elements, with the exception of O and Si. It is not found in the metallic state, but exists as silicates in various clays, in the topaz, garnets and feldspar; as a hydrated phosphate in the turquoise; as an oxide in corundum, in the sapphire, ruby, emery, etc., and in bauxite, from which it is prepared commercially.

The method of preparation consists in powdering the bauxite, freeing it from water and organic impurities, and heating it with caustic soda solution under high steam pressure. By the addition of alumina, aluminium oxide or alumina is then precipitated from the product in the form of a hydrate. The final process is the re-



duction of alumina by electrolysis. A substance called cryolite, which is a compound of aluminium, sodium and fluorine, melts at a low temperature and easily dissolves alumina. A molten mixture of the two is connected with one terminal of an electric generator, and the current is introduced into the mass by means of a number of carbon rods dipping below the surface. Decomposition by electrolysis results, and the aluminium collects in molten form at the bottom of the mass, from whence it is drawn off. The reaction taking place is usually expressed as:



**Properties.**—Aluminium is silver-white in color, almost as hard and tenacious as steel, and ranks next to copper as a conductor of heat and electricity. It can be drawn to extremely fine wire and beaten to a film  $\frac{1}{40000}$  of an inch in thickness. A film of oxide which forms on its surface is protective. Its specific gravity is only 2.6, and its melting point  $600\text{--}700^\circ$ .

Aluminium is readily reactive with alkalis and hydrochloric acid, and slightly so with organic acids, an action which is increased if sodium chloride is present or if the metal is tarnished. On account of its lightness it is much in demand for cooking utensils, but care must be taken that it does not come in contact with caustic alkalies. It discolours readily, and should be cleaned with a neutral scouring powder, or neutral soap and ammonia. Oxalic acid in hot dilute solution will remove any dis-

coloration but will soon roughen the surface of the metal.

Several alloys of aluminium are known, the principal ones being bronzes. The true aluminium bronzes are compounds of Cu and Al alone, but various other metals such as Zn, Ni, and Mg, are also introduced. Aluminium has been added to brass with good effect. Other alloys are combinations with Fe, Bi, Sn and Ag. Magnalium is a useful alloy containing from 2 per cent. to 10 per cent. of magnesium. It takes a high polish and works well in the lathe.

An alloy of aluminium and copper, called cupror, has been placed on the market recently. It is designed to take the place of silver for flat tableware, trays, bowls, pitchers, etc. The color of the alloy is that of 18-k gold. The properties claimed for the new alloy are a high degree of polish, freedom from oxidation, resistance to acids, durability and cheapness. Articles made of it cost a little less than the best silver plated ware.

Aluminium is of two forms in cooking utensils: cast, and rolled or spun. In the former, copper is added and the utensil is cast in one piece. The spun articles are made from sheets of aluminium rolled to the required thickness and drawn to the desired shape on a machine.

#### EXPERIMENT.

Test bright and tarnished aluminum as in experiment 1, p. 47. Filter. Neutralize the acid solutions with ammonia in the presence of ammonium chloride and the alkaline solutions with HCl. Note the precipitates and write the reactions.

Silver is found native with copper and gold, and also

as a sulphide, associated chiefly with galena (lead sulphide). Small amounts are obtained from antimony and arsenic compounds, and in the form of silver chloride.

In the electrolytic refining of copper (p. 51) silver is separated from the bath. The principal methods of extracting silver from its ores are (1) amalgamation; (2) lixiviation; (3) smelting.

In the amalgamation process the chloride, bromide, etc., are brought into prolonged contact with mercury, which reduces the silver from its compound and forms an amalgam with it. Complex sulphides of silver resist amalgamation and must have a preliminary treatment consisting in roasting the ore with common salt or with copper compounds to produce silver chloride. This was the patio process used in Mexico for 350 years, and only recently superseded by the cyanide process, described under lixiviation.

In the lixiviation processes the silver is dissolved from its ores by aqueous solutions and is precipitated as the metal or as a sulphide. The cyanide method is the most important. It is a complicated process. In brief, the ore is crushed fine, mixed with cyanide solution, and the pulp kept in contact with the solution until the dissolution of the silver is complete. The mass then passes into vacuum filters, and silver is precipitated from the clear filtrate by either zinc dust or zinc shavings. Smelting with nitre follows. The silver thus produced is impure, and is carried through a refining process.

Smelting is a process applied to silver ores containing

large percentages of lead and copper. From the blast furnace the silver comes out associated with lead as pig lead or "base bullion." The amount of silver is seldom over 2 per cent. It is separated from the lead by the process of zinc desilverization and cupellation. Zinc and lead are quite insoluble in each other and silver is more soluble in zinc than in lead. Taking advantage of these facts, the process is operated as follows: silver lead is melted in large cast iron kettles and the zinc added and well stirred. On standing and partially cooling, the zinc, carrying silver and a little lead, rises and forms a crust which is skimmed and heated in retorts to drive off zinc. The residue, lead and silver, is then heated in a reverberatory furnace (cupellation) with bone ash bed. The lead oxidizes, melts and is absorbed by the bone ash, leaving the silver.

**Properties.**—Silver is a white metal, softer than copper and harder than gold. It is highly ductile and malleable, and the best conductor known of heat and electricity. Its specific gravity when cast is 10.5, and its melting point about  $960^{\circ}$ . It does not oxidize readily in air, but is rapidly attacked by sulphides, producing a black coating of  $\text{Ag}_2\text{S}$ .

Oxidized silver is made by dipping silver articles in a solution of potassium hydrogen sulphide, which produces a film of silver sulphide.

Silver dissolves readily in nitric acid, is somewhat reactive with most other mineral and organic acids, but not at all with alkalies.

In order to harden silver, it is alloyed with copper in the following proportions: coin silver, 900 parts silver, 100 parts copper, sterling silver, 925 parts silver, 75 parts copper. All solid household silver is now "sterling."

Many silver ornaments contain even less silver, but articles stamped "sterling" are trustworthy. Silver plated ware consists of articles fashioned of German silver or pewter, on which is deposited by electrolysis a triple or quadruple coating of pure silver. The process is similar to copper plating, the silver bath consisting of potassium silver cyanide,  $\text{KAg}(\text{CN})_2$ . The coating has a frosted appearance and needs burnishing or smoothing before use. Since the coat deposited in this manner is pure silver, these articles do not stand as much careless and rough handling as the harder sterling or coin ware, and much of the coating is rubbed off in the process of cleansing with the so-called silver polishes. Plated ware will last much longer if simply washed with hot water and neutral soap. In order to remove the tarnish due to sulphides (eggs), soak the articles in a clean tin or aluminium pan containing enough baking soda solution to cover and let them remain until bright. The soda solution is made by dissolving a tablespoonful of  $\text{NaHCO}_3$  in a quart of tepid water. Or the water may be made to boil over the silver and the soda added.

**Tin**, (Stannum) Sn, occurs in Cornwall and the East Indies as Cassiterite (tin stone),  $\text{SnO}_2$ . The ore is crushed and washed to remove rock, roasted to oxidize sulphide of iron and copper and to remove arsenic, then

leached with water to dissolve sulphate of iron and copper, dried and reduced with coal in a reverberatory furnace.

**Properties.**—Tin is a soft, silver-white, crystalline metal, malleable but not tenacious. It melts at about  $230^{\circ}$ . Its specific gravity is 7.3. On bending bar tin a peculiar crackling sound, called the “cry of tin,” is heard, caused by the friction of interlaced crystals. Pure tin resists oxidation in moist air, and is not quickly susceptible to the action of dilute acids and alkalies. However, there are certain fruits and vegetables which attack the coating of a tin can to some extent, forming salts of tin which are objectionable. A lacquered can is preferable for raspberries, cherries, plums, beets, pumpkin, hominy, etc. On the other hand, cases of poisoning traced to canned foodstuffs may have been caused either by the imperfect condition of the food when canned or by careless soldering. The latter evil is now largely done away with by present methods of sealing tin cans.

Tin plate is made by dipping carefully cleaned sheets of iron or steel in molten tin. It is much used for roofing, household ware and cans for preserving food. Care must always be exercised that tin vessels are not overheated, since the element has a low fusion point and will run off leaving the iron bare, therefore it should never be used in the oven or for broiling, roasting or frying. Liquid mixtures may be cooked in tin vessels without doing any damage.

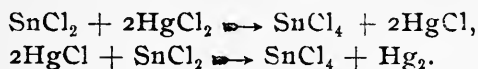
Various useful alloys are known, *viz.*, bronze, soft

solder (half tin, half lead), plate pewter, antimony, bisbuth and copper; Britannia metal, 10 per cent. antimony.

### EXPERIMENTS.

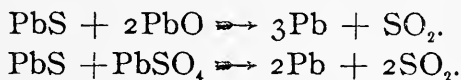
1. Heat a small piece of tin plate over the Bunsen flame, note the crystalline appearance on cooling; treat a piece with moderately strong acid and note a similar effect. Where have you frequently seen this phenomenon?

2. Subject pieces of bright and tarnished tin to the action of dilute acids and alkali as under iron. Test the filtered liquids for soluble tin compounds by acidifying with HCl and adding mercuric chloride. A white precipitate of mercurous chloride results, passing to a gray precipitate of metallic mercury, if sufficient stannous chloride is present, the tin acting as a reducing agent as follows:



Write the reactions for the action of HCl,  $\text{CH}_3\text{COOH}$  and NaOH on tin. (NaOH produces sodium metastannate as the final product.)

**Lead**, Pb (Plumbum), occurs principally as galena, PbS (frequently carrying silver). The metal is obtained by roasting the ore until partially converted into oxide and sulphate. On closing the furnace doors and increasing the heat, the charge is reduced to metal:



Lead is gray in color, soft, of slight tensile strength but very malleable. Melting-point  $325^\circ\text{--}335^\circ$  and specific gravity about 11.3. It is only slightly soluble in acids and alkalies, but its oxide is very soluble. Lead pipes are formed by forcing warm lead through steel dies by hydraulic pressure. They are largely used for conduct-

ing water in the household. The danger of drinking water conducted by lead pipes is much exaggerated. Unless the water is unusually soft, the interior of the pipe quickly becomes coated with insoluble sulphate and carbonate. A wise precaution with new plumbing is to allow the water to run for some minutes before use. Lead enters into many useful alloys previously mentioned.

Lead oxidizes superficially, the compound formed being the black suboxide,  $Pb_2O$ , formerly used in place of graphite for lead pencils.

The crystalline character of lead and some of its compounds can be shown by the following:

#### EXPERIMENTS.

1. Dissolve two small portions of lead oxide, one in dilute  $HNO_3$  and the other in acetic acid; pour a little of each solution in two separate watch-glasses and set them aside to evaporate. Examine the crystalline residue in each case. Scrape two pieces of lead bright and immerse one in strong nitric acid, the other in acetic acid; allow them to stand several days, then examine, and compare with the crystals found above.

2. Immerse bright lead in water charged with carbon dioxide; after several hours standing pour off the water and test it with hydrogen sulphide.

3. Treat small pieces of bright and tarnished lead separately in weak solutions of acids and alkali as under iron. Pour off the clear solutions, acidify with  $HNO_3$  where necessary, and test for lead by passing  $H_2S$  through the liquid. A black precipitate ( $PbS$ ) indicates lead.

*Summary.*—Each student should make a tabular statement comparing the metals of the household with regard to action with acids and alkalies, cost, durability, sus-



ceptibility to oxidation, methods of cleaning, heat properties, etc.

## USEFUL TABLES.

	Heat conductivity	Specific heat
Silver .....	100.0	0.056
Copper.....	73.0	0.094
Aluminium .....	48.0	0.218
Brass .....	23.0	0.086
Zinc .....	19.0	0.093
Tin ... ..	15.0	0.055
Nickel .....	14.0	0.109
Iron .....	11.9	0.115
Steel.....	11.6	0.117
Platinum .....	8.4	0.032
Porcelain .....	0.24	0.2
Soapstone .....	0.2	0.2
Glass .. ..	0.16	0.2
Asbestos .....	0.001	0.194

## CHAPTER V.

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### **GLASS, POTTERY, AND PORCELAIN.**

These materials belong to a series of infusible and insoluble silicates of great utility in all household operations. Glass consists of a mixture of silicates in the amorphous state and is highly prized on account of its brilliancy and transparency; the mass may be colored without affecting either of these qualities. The usual varieties of glass consist of a mixture of alkaline (with alkaline earth) or heavy metal silicates, and are known as Bohemian, Crown, Bottle and Flint glasses.

Bohemian glass is a silicate of potash and lime. It is very infusible and insoluble, therefore especially adapted for chemical purposes.

Window or Crown glass is a silicate of soda and lime. It is more fusible but harder than the Bohemian and is more easily affected by acids.

Bottle glass is an impure variety of the above, colored with iron.

Flint glass is a potash lead silicate. This is the most fusible kind of glass and is easily attacked by chemical reagents; on account of its high refractive power, it is much used for optical purposes.

All kinds of glass are prepared by fusing more or less pure silica in the form of sand or powdered quartz with the potash or soda and lime or red lead, for many hours in large earthenware pots, heated in appropriate furnaces. When the mass has cleared, it is cast or blown and cooled rapidly in order to retain its transparency.

Annealing is a process of heating to a temperature short of softening and cooling slowly, thereby reducing the brittleness.

While transparency is a very important property of all glasses, there are several useful opaque forms. Opaque glass is the result of suspending finely divided infusible material in the molten mass. Such materials are bone phosphates, cryolite, zinc or tin oxides, etc. The enamels used on cooking utensils are of similar composition, and should be handled with the same care as glass articles. On account of the great difference in the expansion coefficients of the glaze and metal base, too sudden cooling or heating of the utensil should be avoided. Likewise judgment and care should be exercised in the selection and use of cleansing agents. Pure neutral soap is the best medium to employ, and under no circumstances is the use of strong caustic alkalies or sharp abrasives justified.

One of the most characteristic properties of all glasses is the solvent effect of hydrofluoric acid and soluble fluorides. Etching on glass is largely accomplished by this means.

Colored glass is the result of dissolving some appropriate mineral oxide in either variety of glass:

Ruby—oxide of gold or copper.

Topaz—sulphide of antimony.

Yellow—silver chloride or borate.

Green—oxide of chromium.

Blue—oxide of cobalt.

Amethyst—oxide of manganese.

### EXPERIMENTS.

1. **Corrosive Action of Alkalies.**—Half fill common prescription bottles (4 oz.) with strong caustic soda solution. Place them in warm salt water, bring slowly to a boil and continue for at least 1 hour, then cool slowly, pour out the contents, rinse with clean water and examine the inner surface.

2. **Etching Tests.**—(a) With a clean steel pen and dilute hydrofluoric acid, HF, write your name and the date on a clean microscope slide.

(b) Thinly cover a clean watch-glass with warm paraffin. When cool cut your name with a pencil point through the paraffin and immediately invert over a lead dish containing a mixture of fluorspar and concentrated sulphuric acid. After half an hour's gentle heating, rub off the paraffin and examine the result.

3. **Detection of Arsenic, Lead, Etc.**—Fuse finely ground chips of kitchen utensil enamel with an excess of potassium sodium carbonate in an iron or nickel crucible, cool and extract the melt with hot water. Filter and wash the residue several times with hot water. Test the filtrate for arsenic, lead, and acids, by dividing it into 3 parts—two of one-quarter each and the third the remaining half.

Part I. Test for arsenic by making strongly acid with HCl and boiling with a strip of clean copper. A gray or black coating indicates arsenic.

Part II. Make acid with HCl and pass  $H_2S$  rapidly through the solution. A black precipitate indicates lead.

Part III. One-half of the solution—tests for sulphates, borates, phosphates, and silicates, as follows:

Neutralize with HCl, if any precipitate forms, filter and divide the filtrate into 3 parts. The residue is silicates. Take 1 part of the filtrate, thoroughly moisten a strip of turmeric paper with it and dry at  $100^\circ C$ . A pink color indicates borates.

To another part, add barium chloride and a few drops of HCl. A white crystalline precipitate indicates sulphates. Pour a few

drops of the remaining part into an excess of ammonium molybdate. Warm gently and a yellow color or yellow crystalline precipitate indicates phosphate.

*Porcelain and Pottery* are fused silicates of alumina, the former pure, and the latter contaminated with oxides of iron, manganese, etc.

The primary source of these wares is clay, a highly infusible hydrated silicate of alumina. For porcelain making it is mixed with some fusible silicate such as feldspar, and a small quantity of water, moulded into shape, dried and heated in a furnace for many hours. The feldspar or flux only melts and running through the porous mass cements it together. Even after firing, the ware requires coating with the glaze, a mixture of slightly fusible material suspended in water into which the article is dipped. It is dried and returned to the furnace for heating. The glaze is, in effect, a true glass and makes the mass impenetrable to liquids. Decorative effects are produced in two ways, called under- and over-glaze, of which the former is the better and more permanent. For under-glaze work, finely ground colored glass suspended in turpentine is applied to the unglazed ware and afterwards "fired" at the high temperature of the porcelain furnace. The glaze is subsequently applied and fired as before. Over-glaze decoration admits of the use of colors which may be injured by the high heat of the porcelain furnace and is applied at a lower temperature in a muffle. The colors consist of various oxides mixed with borax, litharge, nitre, etc. They are applied in watery solution.

Stoneware is an impure form of porcelain, somewhat more fusible and usually glazed with borax. The finer qualities are known as china. Earthenware and brick consist of clay and sand, mixed with water, moulded, dried and fired in a kiln. The former is usually glazed with salt, while the latter is left in the porous state.

Since most of our decorated table china is over-glaze ware it is likely that it will not successfully withstand repeated washings, especially since modern practice has brought into use many forms of alkaline detergents, *i. e.*, soap powders and cleaners. Some of these contain bleaching agents, which liberate chlorine and are therefore destructive to gold, but prolonged contact with the strong alkalies in their composition is sufficient to hasten the removal of both gold and color decoration.

### EXPERIMENTS.

1. Heat several decorated dishes in new enameled saucepans with solutions of various soaps and other cleansers. Keep the pans covered and boil gently for 1 hour. Cool, rinse in clear water, and examine the effect, both on the china and the saucepan.

2. **Porosity.**—Weigh small pieces of dry unglazed porcelain and earthenware, soak over night in water, wipe dry and weigh again. Calculate the per cent. of water absorbed.

3. **Fusibility.**—Heat small splinters of porcelain and earthenware held in platinum wire (spiral) at the highest heat of your burner. Cool and examine with a magnifier. Are the edges sharp or rounded?

4. **Testing for Lead in the Glaze.**—Boil the article for some time in caustic soda, cool the liquid and add  $(\text{NH}_4)_2\text{S}$ . A darkening of the liquid or a black precipitate due to lead sulphide,  $\text{PbS}$ , indicates lead.

## CHAPTER VI.

### FUELS.

Fuels are materials used for producing heat; they must be capable of uniting with oxygen under easily obtainable conditions and of evolving much heat energy during the process of combustion. Occurring as gases, liquids and solids, carbon and its compounds largely fill the required conditions.

**Classification.**—A logical arrangement of the fuels would result as follows:

Pure fuels	Gases	{	Natural	{	Hydrogen
				{	Hydrocarbons
	Liquids	{	Artificial	{	Carbon
				{	monoxide
		{	Natural	{	Hydrocarbons
				{	Hydrocarbons
Impure fuels	Solids	{	Artificial	{	Alcohols
				{	Hydrocarbons
	Solids	{	Natural	{	Anthracite
				{	Coke
		{	Artificial	{	Charcoal
				{	Soft coal
	Solids	{	Natural	{	Peat
				{	Woods

Coals, petroleum and natural gas are evidently of plant and animal origin, produced by a natural method of decomposition, similar to a process of dry distillation.

The terms pure and impure are used in a restricted sense, the former signifying that the substance is ready for direct combustion, while in the latter case a number of complicated chemical changes must take place before

combustion is possible. This is explained in detail in the discussion of the composition of wood.

**Historical:** Woods both hard and soft and charcoal have been used from the earliest times. Peat, a form of partly carbonized turf, was the main fuel of European countries during the Middle Ages and is still in use. Soft coal came into use during the 15th century, while gas and hard coal were first employed in the early part of the 19th century, and hydrocarbons about the middle of the same epoch. Alcohol is just coming into general use in our own times.

Impure solid fuels on account of more extended use will be first discussed.

**Wood, peat and soft coal** are such impure forms of fuel and must undergo so many and such complicated chemical changes before they are capable of yielding heat, that their actual fuel value is frequently over-estimated and rarely understood by the consumer. The following is a brief and simple statement of composition and changes to be expected:

*Wood* contains, moisture,  $(\text{H}_2\text{O})$ ; resin,  $(\text{C}_x\text{H}_x)$ ; starch, gum, and cellulose,  $n(\text{C}_6\text{H}_{10}\text{O}_5)$ ; oil,  $(\text{C}_x\text{H}_x\text{O}_x)$ ; mineral matter or ash.

Considerable heat is required to drive off the moisture and raise the starch, cellulose, etc., to such temperatures that they will decompose, yielding gases of a combustible nature, for example  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{H}_2$ ; in this decomposition  $\text{H}_2\text{O}$  is formed and must be driven off as a gas. Much heat is also absorbed by the ash in forming new chemical compounds. In fact the fuel effi-



ciency of wood depends entirely upon the relative volumes of combustible gas and charcoal furnished, and as the charcoal or carbon is the best solid fuel, the wood furnishing the largest proportion of carbon in this form is the best fuel, hence we find it advantageous to use hardwood. It must be understood that carbon or charcoal at a red heat combines with a limited amount of oxygen and forms a combustible gas, carbon monoxide, CO, a fuel of the highest heating efficiency.

*Soft coal*, a partly carbonized plant product, produces less water by chemical change and yields the combustible gases and carbon (coke) in larger proportion.

*Hard coal* is superior to soft, since it is a purer form of carbon and yields very little combustible gas.

#### EXPERIMENT.

To determine the value of coal or wood for fuel purposes, proceed as follows: Take 1 gram of pulverized coal or small pieces of wood in a weighed crucible, dry at  $120^{\circ}$  with cover off, cool and weigh; the loss is water. Heat the crucible with cover on in a strong Bunsen flame for 7 minutes, cool and weigh; the loss is volatile combustible matter (tar, smoke, etc.). Heat again with cover off until nothing remains but ash. This operation will require some time; cool and weigh; the loss is fixed carbon (actual fuel). Subtract the weight of the crucible; the difference is ash.

The quantity of ash in coals is always greater than in wood, owing to the presence of foreign mineral substances such as silica, lime and sulphide of iron derived from the earthy strata in which the coal is deposited.

Flue dust, collecting in stove pipes and flues where hard coal is burned, contains sulphate of ammonia.

When cool, this salt absorbs water and attacks iron, rapidly corroding the pipes. This fact explains the necessity of cleaning the smoke pipes of furnaces and stoves in the spring of the year when the heating apparatus is no longer used.

#### EXPERIMENT.

Collect some of the light gray dust from a smoke pipe, treat about 1 gram with boiling water on a filter, pouring the liquid through several times. Reserve the residue and test the liquid in the usual manner for ammonia and sulphates. Extract the residue still on the filter-paper with boiling dilute  $\text{HCl}$  until the residue is light in color. This is mainly silica from the coal ash. Test the acid filtrate for ferric iron and lime in the usual manner.

**Liquid Fuels.**—These comprise alcohols, and hydrocarbons in the form of gasoline or naphtha, and kerosene. The hydrocarbons are highly inflammable liquids obtained from crude petroleum.

The distillation of petroleum was carried on in Europe early in the 18th century, and there is evidence of the use of the crude oil by fire worshippers as far back as Zoroaster. The great oil region of Europe is the Baku peninsula on the Caspian Sea. Crude petroleum was known to the Indians in America, and in New York State it became popular as a specific for rheumatism, under the name of Seneca Oil. Refined petroleum in the United States dates from 1855, when it was distilled and put on the market as a patent medicine called American Oil. Up to this time a limited quantity had been obtained at or near the surface of the ground. In 1859, in Titusville, Pa., Col. Drake applied the method of

boring artesian wells to obtain petroleum from underlying strata, and the industry was revolutionized. In that year 2,000 barrels of crude petroleum were produced, 2 years later 2,000,000, and in 1910 210,000,000 barrels. The new supply gave a material more profitable for refining than shale oil. By fractional distillation at first, a number of distillates were obtained ranging from petroleum ether, naphthas, gasoline, etc., to solid paraffins. The yield of gasoline by this process was entirely insufficient, however, to meet the sudden demand created by the automobile and motor engines, so a system of "cracking" was devised, which has greatly increased the light oil distillate, and is better suited to the refining of oils from the newer western fields.

**Cracking Process.**—This is a method of distilling at a temperature higher than the normal boiling points of the constituents to be obtained, which effects a dissociation of many of the heavier oils into lighter hydrocarbons. As the process is conducted in some places, the charge of oil (about 1,000 barrels) is put into a side-firing still, the temperature is raised to 600° or 700° F., and the vapors as they come off are carried to a series of condensers, where they are separated, the heaviest vapors condensing first, the lightest traveling farthest before being condensed. The vapors of a considerable amount of the oil intermediate between kerosene and lubricating oils are returned to the still, superheated, and decomposed, so increasing the yield of light distillate. Usually 3 streams of oil of different specific gravities

are simultaneously received: the heaviest, or the paraffin oil distillate; the intermediate, or gas oil, and the light oil distillate. The paraffin oil distillate is worked up to produce lubricating oils, paraffin, etc., the intermediate distillate is refined for burning and gas oils, and the light distillate is fractionally distilled and yields a number of important compounds, such as:

Cymogene, specific gravity  $110^{\circ}$  Baumé. Used in the manufacture of ice.

Rhigolene, specific gravity  $100^{\circ}$  Baumé. Used as an anaesthetic.

Petroleum ether,  $85^{\circ}$ - $80^{\circ}$  Baumé. Used as a solvent and for carbureting air in gas machines.

Benzine,  $89^{\circ}$ - $82^{\circ}$  Baumé. A solvent.

Gasoline. Varies widely in specific gravity and quality, according to the demand. It may have a specific gravity of  $80^{\circ}$ - $60^{\circ}$  Baumé.

For the purification of petroleum products the use of sulphuric acid followed by soda lye is universal. Aromatic hydrocarbons, fatty and other acids, phenols and tarry bodies are thus decomposed or removed. Sulphur compounds are taken out in the form of sulphides by copper.

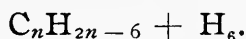
**Chemical Nature of Petroleums.**—Crude petroleum from different fields shows great differences in chemical constituents. The Pennsylvania petroleum yields hydrocarbons of the methane series principally, compounds from  $C_4H_{10}$  to  $C_{35}H_{72}$  having been isolated in almost unbroken sequence, with many of their isomeric forms.

Ring hydrocarbons such as benzene,  $C_6H_6$ , have also been found in smaller quantity.

The California oils are of varied character and consist of a more or less dense asphaltic base. Asphalt is usually regarded as evaporated and oxidized petroleum. Phenols are common constituents; nitrogenous ring compounds and the olefines from  $C_2H_4$  to  $C_{30}H_{30}$  inclusive have been obtained. The California field is very active, a single well having made a record of 30,000 to 60,000 barrels per day.

The Texas oil seems to combine the characteristics of the Pennsylvania and the California types, while the mid-western field produces both kinds.

Russian and Cuban petroleum consist largely of the unsaturated hydrocarbons of the naphthene series,



The depth at which petroleum is found is of interest. In Pennsylvania wells range from 300 to 3,700 feet; in California they have been drilled to a depth of over 4,000 feet.

**Products of Combustion.**—At temperatures slightly above normal liquid fuels readily combine with oxygen, producing intense heat and yielding water and carbon dioxide as products but no ash; with too small supply of oxygen the temperature of combustion is much lowered and a large part of the carbon is not consumed and escapes in a free state, producing a yellow flame and if in great excess much black smoke—a very familiar phenomenon in kerosene lamps.

With great excess of oxygen, as when the hot vapor of these liquids is mixed with many times its volume of air, in a confined space, the combustion is so rapid as to produce an explosion (automobile engine). When using these products for fuel purposes care must be taken that these last conditions do not exist. Hence as a measure of safety the lamp or stove reservoir is kept well filled and cool. The following simple experiments will serve to impress these important facts on the student's mind:—

#### EXPERIMENTS.

1. Pour not more than 1 or 2 drops of clean gasoline into a clean, dry, wide-mouth bottle of 12 to 16 ounces capacity, stir the vapor for a moment with a hot glass or iron rod and bring a lighted match over the mouth of the bottle; a slight but perceptible explosion should result with or without blue flame.

2. Pour a teaspoonful of the same liquid in a shallow porcelain dish or saucer, apply the lighted match and note the yellow flame, but no explosion. Quench by covering with cloth, stiff cardboard or any article that will exclude air.

Gasoline is used quite largely in some localities as a source of heat, being consumed in the so-called blue flame stove, which operates by heating the liquid to such a temperature, air being excluded, that vapor forms rapidly and under slight pressure. It is then conducted to the burner (Bunsen), mixed with the proper amount of air, and burns with a blue flame. These stoves and heaters are perfectly safe as long as they are kept clean, do not leak liquid, are kept well filled and furnished with good gasoline. The quality of gasoline may be determined by the following tests:

1. Observe the color, it should be white as water.
2. Clearness; if cloudy, dirt or water is present. Evaporate a small quantity in a clean porcelain dish over warm water (no flame) and examine the residue; also filter some through clean dry chamois skin. Water and dirt will remain on the skin. It is a wise precaution for users of gasoline for any purpose to filter as above before using.
3. Test with delicate litmus paper; it should be neutral.
4. Determine the specific gravity with the Baumé hydrometer for light liquids; it should register not higher than  $72^{\circ}$  for fuel purposes.

Kerosene, erroneously called an oil, is much more extensively used and widely known; it is probably the cheapest and best liquid illuminating agent of the present day. The ordinary kerosene wick lamp is so well known as to need no explanation. Kerosene, however, is used in blue flame stoves, such as the Khotal, etc., and although more troublesome to manipulate is preferred by most people because the danger is minimized.

Kerosene should successfully stand tests 1, 2, 3, given under gasoline. The specific gravity should be  $48^{\circ}$  Baumé.

In addition, flash and fire tests are prescribed in most parts of the world. The former signifies the temperature at which the oil gives off ignitable vapor, and the latter the point at which it takes fire. The experiment below represents the open-cup method of determining the flash point, the figures of which are always slightly lower than by other methods:

Half fill a 200 cc. beaker with kerosene, place over warm water, stir gently with an accurate Fahrenheit thermometer and heat slowly not more than  $2^{\circ}$  rise per minute, until a small open

flame brought over the surface of the oil causes a blue flame and slight explosion. Note the temperature, it is the flash point and should not be lower than 100° F. Air currents and draughts should be excluded in this experiment.

Kerosene and gasoline are unsaponifiable. Prove this in the case of kerosene by the following:

Heat a small quantity of kerosene with one-seventh its volume of a solution of sodium hydroxide (38° Baumé) over hot water, stirring often. On cooling, does the product resemble soap? Is kerosene rightly called an oil?

The increased efficiency of kerosene as a burning fluid in recent years is partly due to the presence in its composition of unsaturated hydrocarbons, formed during the cracking process. These have a higher illuminating power than the former saturated type found in the oil.

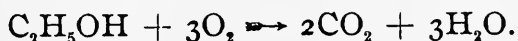
**Alcohols.**—Of this series, only methyl or wood alcohol and ethyl or grain alcohol are used as fuels. A mixture of the two (90 parts ethyl, 9 parts methyl + 1 part benzine) has come into general use under the name of denatured alcohol; it is essentially ethyl alcohol. Methyl alcohol,  $\text{CH}_3\text{OH}$ , is produced commercially by the dry distillation of wood and is known as pyroligneous or wood spirit; it contains light wood tar, acetone, and acetic acid, which should be completely removed before using, leaving a bland mild-smelling liquid similar to ethyl alcohol, known as Columbian Spirit. Much of the ordinary wood alcohol is quite impure. Tar and acetone are easily distinguished by the color and odor, especially if gently heated; acid is readily shown by litmus paper.

As a burning fluid methyl alcohol is distinctly inferior



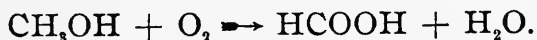
to grain alcohol. The following equation shows the chemical change during complete oxidation:  $2\text{CH}_3\text{OH} + 3\text{O}_2 \rightleftharpoons 4\text{H}_2\text{O} + 2\text{CO}_2$ .

In stoves or lamps of the best type, ethyl or grain alcohol burns as follows:



Comparing this equation with that of methyl alcohol it will be seen that the amount of  $\text{CO}_2$  is doubled, hence it is fair to assume that the heating effect is greater; ethyl alcohol is less volatile than methyl, therefore loss by evaporation during use is less.

Methyl alcohol is readily oxidized to formaldehyde by means of hot copper oxide (see Experiment I, p. 52). This serves as a test for the identification of this alcohol. By further oxidation methyl alcohol yields formic acid:



Ethyl or grain alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , is prepared by the fermentation of glucose or maltose by means of yeasts and distillation of the product. It is a colorless liquid with pleasant and characteristic odor, usually containing about 95 per cent. of pure alcohol and the balance water and small amounts of impurities, acetic acid and acetone more especially; these are not particularly objectionable if the liquid is to be used for generating heat or general solvent purposes, but in many chemical operations further purification is necessary. Pure alcohol, free from aldehyde and acid for chemical purposes, can easily be made from the ordinary 95 per cent. variety or even waste alcohol by allowing it to remain for several days

in contact with slightly rancid tallow or grease and subsequently filtering, distilling and neutralizing the product.

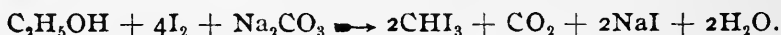
On account of the high price, due to the government tax, ethyl alcohol was formerly little used for heat and power purposes, but since the introduction of denatured alcohol, the cost has fallen to 50 cents per gallon and the use enormously increased. At the present price, it is little more expensive to use than gasoline and far safer and pleasanter to handle.

### EXPERIMENTS.

1. Determine the boiling point of 95 per cent. ethyl alcohol by distilling 100 cc. in a small flask fitted with a thermometer and condenser.

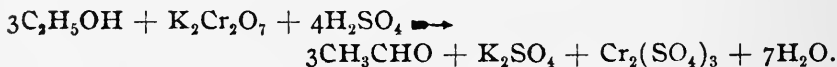
2. Determine the specific gravity of alcohol by means of the hydrometer and check the result by the Westphal balance.

3. Ethyl alcohol combines with iodine in the presence of strong alkali, forming iodoform:



To 3 cc. of  $\text{C}_2\text{H}_5\text{OH}$  and an equal amount of tincture of iodine in a test tube, add  $\text{Na}_2\text{CO}_3$  in small amounts, shaking after each addition and warming gently until the solution is just decolorized and yellow crystals of iodoform appear. About 5 cc. of  $\text{Na}_2\text{CO}_3$  will be used.

4. By the use of an oxidizing agent such as  $\text{K}_2\text{Cr}_2\text{O}_7$ , ethyl alcohol is converted into acetaldehyde:



Heat 10 cc. of alcohol with 1 cc. of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution acidified with sulphuric acid, notice the reduction of the chromium to base and the odor of aldehyde.

5. Since ethyl alcohol oxidizes readily to acetic acid, some acidity is found in most samples. The amount may be such as

to cause corrosion of metal containers or burners in alcohol stoves.

Determine the acidity of 10 cc. of alcohol with N/10 alkali, calculating the percentage in terms of acetic acid.

**Gases.**—Gas consisting of hydrogen, carbon monoxide, and various hydrocarbons is the ideal fuel. There are seven varieties in use for fuel and lighting purposes, *viz.*:

Gases proper	{	Natural gas
		Water gas
		Coal gas
		Acetylene gas
		Blau gas
Naphtha or air gas	{	Pintsch gas
		Cold air charged with naphtha vapor.

**Natural gas** has been found in large pockets in the earth in various localities for many years. The shrines of antiquity were in some cases supplied with gas from crevices in the earth; it is probable that the temple of Diana at Ephesus had a natural gas well.

Fredonia, N. Y., was lighted with natural gas as early as 1825. The supply was accidentally discovered when boring for salt, as these earth pockets are reached by drilling as for oil or brine. The gas comes out under tremendous pressure, which must be controlled and reduced for household use. Its main constituent is methane or marsh gas, which has little or no illuminating power, but is an excellent source of heat. The supply of natural gas from earth pockets is gradually becoming exhausted.

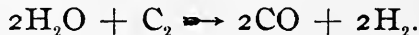
Three classes of natural gas are recognized:

(1) The gas which issues from marshy beds, and contains methane as its only combustible constituent.

(2) Natural gas found in pockets occurring in oil fields but not associated with oil. In this, methane predominates, but hydrocarbons higher in the series are found. This is the gas which supplies Pittsburgh and Cleveland.

(3) A gas associated with petroleum, called "wet" gas, from which gasoline can be obtained. Natural gas of this type is found in almost every oil-producing state of the union. By compressing this gas to 350 pounds per square inch, and passing it through cooled condenser coils, a gasoline is produced with specific gravity of  $77^{\circ}$  to  $110^{\circ}$  Baumé. Being extremely volatile, it is kept in tanks under heavy pressure, and when drawn off is usually mixed at once with low grade refinery naphthas. The amount of gasoline obtained in the last few years from natural gas has approximated 10,000,000 gallons annually. The residual gas left after the gasoline extraction has a high heating value and is utilized for that purpose.

**Water Gas.**—By passing steam at high pressure over incandescent carbon a mixture of hydrogen and carbon monoxide, known as water gas, is produced. The carbon used may be in the form of anthracite, coke, or even charcoal. A high temperature is necessary for the operation, usually about  $3,000^{\circ}$  F. Decomposition takes place, the chemical change being as follows:



In order to give the resulting gases illuminating quality

they are mixed with light hydrocarbons and the combination passed through a red hot zone. The naphtha vapors are broken up (cracked) into permanent gases such as methane, ethylene and acetylene, giving the product a composition similar to coal gas (q. v.) but combined in somewhat different proportions. Since it contains more carbon monoxide it is generally regarded as a better fuel.

**Coal Gas.**—From soft or bituminous coals, a gas can be produced by dry distillation. This was the first method used for making gas, and dates back to early days of the 19th century. On account of the many and valuable by-products produced, *viz.*, ammonia, coal tar, carbolic acid, naphthalene, cyanides, etc., it will probably be used for many years to come.

The process consists in heating the coal in large clay retorts, drawing off and cooling the gas in order to condense tar, washing to remove ammonia, tar, etc., removing sulphur with lime or iron oxide, storing and delivering the gas under slight pressure. Essentially the same process of purification is used with water gas. In recent years the horizontal retort for the distillation of the coal has been generally superseded by the inclined or vertical type. The charge of coal is admitted at the top and the retort filled. When the distilling process is complete, the bottom of the retort is opened, and the residue, coke, falls out by gravity.

The changes which take place when soft coal is thus burned out of contact with air are extremely compli-

cated. The products formed are gaseous, liquid, and solid. The liquid constituents which condense as coal tar yield on further treatment a number of substances such as benzol and anthracene, which are the basis of thousands of important organic compounds. The gaseous products, which are combined as illuminating gas, are conveniently classified as follows:

Impurities or diluents—oxygen, carbon dioxide, nitrogen.

Illuminants—ethylene, acetylene.

Gas proper—hydrogen, marsh gas or methane, carbon monoxide.

Hydrogen sulphide is the only impurity in gas of any importance; by its combustion sulphur dioxide and water are produced, finally resulting in sulphurous acid, which readily attacks fabrics and metals and bleaches many colors. Any hydrogen sulphide escaping combustion blackens lead acetate paper held far enough above the flame to be uninfluenced by the heat.

Analyses of gas are given below:

	Water gas per cent.	Coal gas
Carbon dioxide .....	0.0	0.0
Illuminants .....	12.6	6.5
Oxygen .....	0.9	0.9
Carbon monoxide ... ..	27.3	6.8
Hydrogen .....	27.7	41.1
Marsh gas.....	27.7	41.0
Nitrogen.....	3.8	3.7
	100.0	100.0
Candle-power .....	25.4	21.32

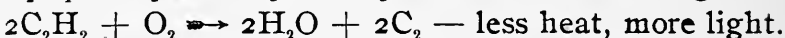
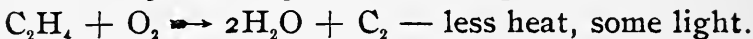
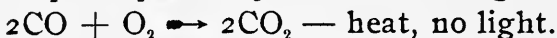
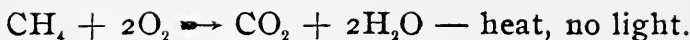
In a water gas, the candle-power is usually double the illuminants.

The value of gas is expressed as candle-power, the unit being a standard sperm candle burning 2 grains per minute; hence a 25-candle-power gas would give as much light as 25 of the candles burning simultaneously. The calorific value of the gas should also be determined as a measure of its quality for general purposes.

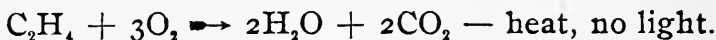
The standard illuminating burner consumes 5 cubic feet per hour under a pressure of  $1\frac{1}{2}$  inches of water. This is used as a unit in all gas calculations.

Two styles of meters are used—the wet and the dry; in the former the gas passes through a revolving drum partially submerged in water. The revolutions are registered on dials by appropriate clockwork. Since this form of meter is liable to freeze and must always contain water, some of which is lost by evaporation, it has been largely superseded by the dry meter, which contains 2 bellows alternately full and empty. A clockwork device, similar to that used in the wet meter, keeps record on appropriate dials. Gas meters are subject to public test and are allowed an error of 2 per cent. either fast or slow.

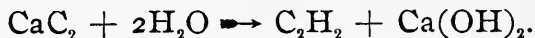
**Chemical Changes During Combustion.**—The common burner can only use gas of the following composition: methane,  $\text{CH}_4$ , ethylene,  $\text{C}_2\text{H}_4$ , acetylene,  $\text{C}_2\text{H}_2$ , hydrogen,  $\text{H}_2$ , and carbon monoxide,  $\text{CO}$ . Combustion proceeds according to the following equations:



The Bunsen burner mixes the gas with  $\text{O}_2$  before combustion; this affects only the ethylene and acetylene as follows:



Acetylene gas,  $\text{C}_2\text{H}_2$ , is made by the action of water on calcium carbide as follows:



Calcium carbide is prepared by heating a mixture of lime and charcoal in the electric furnace.

Either the water is sprayed on the carbide, or finely pulverized carbide is sprinkled in water.

Acetylene is only used in places where ordinary gas cannot be obtained, and is generally used at once. It may, however, be stored in an ingenious manner: strong copper cylinders are partly filled with acetone, and acetylene pumped in until a certain pressure is obtained. By attaching one of these tanks to a lamp, a strong light may be maintained for many hours. The rationale of the process is that acetone dissolves acetylene under pressure and slowly gives it up when the tension is released.

**Naphtha or Gasoline Gas.**—Many isolated country houses depend for heat and light on this mixture. Out-



side of the building and underground, is placed an iron tank for holding the hydrocarbon; pipes lead to and from the house. In the house cellar is placed a large revolving drum driven by weights, for forcing air through the gasoline and driving back to the house the vapor laden air. The process is satisfactory on a small scale but rather expensive, depending wholly on the price of the hydrocarbon.

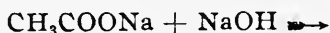
**Blau gas** is the invention of a German chemist, Herman Blau. It is a mixture of hydrocarbons which are gases under ordinary conditions, but which liquefy under high pressures and low temperatures and are reconverted into gases when the pressure is released. In the making of Blau gas ordinary gas oil is distilled in retorts, the mixture of gases produced is purified, cooled and compressed up to 100 atmospheres. Hydrocarbons which liquefy under these conditions will absorb others which do not, and also so-called permanent gases such as methane and hydrogen. The liquefied gas is delivered for use in steel cylinders under high pressure, with a device attached for reducing the pressure before the gas enters the service pipes. One cubic foot of the liquefied substance expands to 400 cubic feet of gas.

**Pintsch Gas.**—A similar method of compressing gas was invented by Pintsch. Under his system the oil is distilled at about  $1,000^{\circ}$ , in order to produce a large amount of fixed gases. About 80 cubic feet of gas is obtained from 1 gallon of oil. These gases are stored in receivers under a pressure ordinarily of 6 atmos-

pheres. Pintsch gas is widely used for lighting railway cars, the receivers being carried underneath the car.

### EXPERIMENTS.

**Preparation of Methane.**—In a hard glass 8-inch test tube place a mixture of 6 grams of *fused* sodium acetate and 4 grams of soda lime. Close with a cork bearing a glass exit tube. Heat strongly and light the methane gas at the mouth of the tube. Complete the equation:



**Preparation of Ethylene.**—To 10 cc. of  $\text{H}_2\text{O}$  in a beaker slowly add 30 cc. of concentrated  $\text{H}_2\text{SO}_4$  and cool. Put 14 cc. of  $\text{C}_2\text{H}_5\text{OH}$  in an Erlenmeyer flask, fitted with a separatory funnel and a delivery tube. Add clean sand to prevent bumping. Carry the delivery tube through the cork of a clean, dry, 12-ounce or 16-ounce bottle. Pass another delivery tube out of the bottle and carry to a pan for collecting gas over water. Slowly pour the cold dilute acid on the alcohol through the funnel, heat gently, and collect 1 wide mouth bottle and 2 narrow necked bottles of the gas. Test the gas in the wide mouth bottle for inflammability. Write the reactions for the preparation of the gas and its combustion.

Into one of the narrow necked bottles place 1 cc. of bromine water, close the bottle and shake. Explain, note odor, and write reaction. Into the second bottle put a very dilute solution of  $\text{K}_2\text{Mn}_2\text{O}_8$  and add 1 cc. of 10 per cent.  $\text{Na}_2\text{CO}_3$ . Close and shake. Note the change. Look up von Baeyer's reaction for the double bond.

**Preparation of Acetylene.** 1.—Drop a very small lump of calcium carbide into a test tube half full of water. Light the gas evolved and note its illuminating quality.

2. Put 10 grams of calcium carbide in an Erlenmeyer flask provided with a separatory funnel and a delivery tube. Add water drop by drop through the funnel and collect the gas evolved over water, in small bottles or cylinders. Observe its

inflammability (Caution: acetylene mixed with air is explosive), its odor, and solubility in water and alcohol. Test with bromine water and  $\text{K}_2\text{Mn}_2\text{O}_8$  as under ethylene. Write reactions.

3. Collect some illuminating gas in bottles containing bromine water and  $\text{K}_2\text{Mn}_2\text{O}_8$  respectively, as under ethylene, and shake. Note results. What does this show with regard to certain constituents of the gas?

## CHAPTER VII.

### CARBOHYDRATES.

Carbohydrates are valuable organic compounds representing one of the food principles. They originate in the development of vegetable life, being built up in the cells of all chlorophyll-bearing plants. These compounds contain the elements carbon, hydrogen and oxygen, and with some exceptions are aldehyde or ketone alcohols. The term carbohydrate, signifying carbon, with hydrogen and oxygen in the proportion to form water, has lost its significance, for although important members of the group conform to this arrangement, *e. g.*, sucrose ( $C_{12}H_{22}O_{11}$ ), glucose ( $C_6H_{12}O_6$ ), and starch  $n(C_6H_{10}O_5)$ , carbohydrate bodies are known which do not. Furthermore, acetic and lactic acids which are not carbohydrates have respective formulas of  $C_2H_4O_2$  and  $C_3H_6O_3$ . A better general term is saccharids or saccharoses. The usual classification subdivides the saccharids as follows:

**Monosaccharids.**—Sugars which do not hydrolyse to simpler saccharids. They are alcohols joined with an aldehyde or a ketone group, and in consequence are called either aldoses or ketoses. The number of carbon atoms in the molecule is indicated by the terms tetrose, pentose, hexose, etc., and the full description may be, for example, aldohexose, or ketohexose. The hexoses are the most important members of this group.

**Disaccharids.**—The disaccharids yield two monosaccharid molecules of the hexose type on hydrolysis.

**Trisaccharids.**—Raffinose, the most important example, hydrolyses to three hexoses.

**Polysaccharids.**—These bodies have large complex molecules which hydrolyse to an unknown number of monosaccharid molecules.

The important carbohydrates are classified in detail below:

**Classification and Occurrence.**—

**MONOSACCHARIDS.**

*Pentoses*,  $C_5H_{10}O_5$ . Arabinose, Xylose, etc.

These do not occur free in nature, but result from the hydrolysis of polysaccharids called pentosans.

*Hexoses*,  $C_6H_{12}O_6$ .

*Glucose* or dextrose. Sometimes called grape sugar. Occurs in large amounts in grapes, is widely distributed in other fruits and plants, and is a product of the hydrolysis of most of the di-, tri-, and polysaccharids. Normal blood contains a small quantity, which is greatly increased in diabetes.

*Fructose* or levulose. Sometimes called fruit sugar. Associated with glucose in nature, is a large constituent of honey, and is also a product of hydrolysis of some carbohydrates.

*Galactose*. Has no common name and is not found free in nature. It is obtained by the hydrolysis of lactose, raffinose, and the galactans.

## DISACCHARIDS.

The important disaccharids have the formula  $C_{12}H_{22}O_{11}$ . They are:

*Sucrose*. Known as cane, beet or maple sugar, and found with glucose and fructose in the juice of many other plants.

*Maltose*. The malt sugar of germinating grains. Also a product commercially of the partial hydrolysis of starch.

*Lactose*. Known as milk sugar and found in the milk of most mammals.

## TRISACCHARID.

Raffinose,  $C_{18}H_{32}O_{16}$ . Found in the germ of wheat and barley, in cotton seed, and usually in the sugar beet. It is commonly extracted from the molasses from beet sugar.

## POLYSACCHARIDS.

The general expression  $nC_6H_{10}O_5$ ,  $n$  signifying that the molecule is an indefinite multiple of the formula given, is assigned to the hexosans of this complex group. Principal members are:

*Starch*. The most important and widely distributed polysaccharid. It occurs in plants generally, especially in roots, tubers and seeds.

*Dextrin*. Formed from starch by the action of heat alone, or by partial hydrolysis with enzymes or acids. Found in germinating cereals as a transition product.

*Glycogen.* Sometimes called animal starch. It is seldom found in plants, except in certain fungi and in varying amounts in yeast. It occurs in large quantities in the liver of animals and in the muscle of the scallop, and in smaller proportion in the blood and muscles generally.

*Cellulose.* Constitutes the framework of the cell walls of all plant tissues. The cotton fiber is nearly pure cellulose.

*Inulin.* A starch-like body extracted principally from dahlia tubers, but found also in the artichoke and the roots of chicory.

*Galactans.* Occur in the seeds of legumes; yield galactose on hydrolysis.

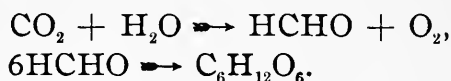
*Pentosans.*  $(C_5H_8O_4)_n$ . Araban and xylan, yielding arabinose and xylose on hydrolysis. Widely distributed in nature, especially in such substances as bran, wood, straw, etc. No considerable amount in food material.

*Natural Gums.* Bodies which are generally classed with the polysaccharids, but the composition of many of which is not definitely known. Pectin bodies belong to this group.

**Photosynthesis.**—In the presence of sunlight the chlorophyll-bearing plant cell takes carbon dioxide from the air, combines it with water, and polymerizes the product into a carbohydrate body. This photosynthesis may be represented by:



Such an expression does not take into account the intermediate products of the synthesis, about which more has to be learned. Baeyer, Erlenmeyer and others theorize that the carbon dioxide and water undergo double decomposition, and formaldehyde is formed and synthesized to a monosaccharid, according to the reactions:



The theory is supported by the fact that formaldehyde has been found in plant cells, and that it can be polymerized to fructose. According to Asher and Priestly, hydrogen peroxide is also produced in the above change, but is quickly decomposed to water and oxygen by a catalase in the leaf.

**Hydrolysis.**—By enzyme action in the plant or animal body, or by the action of dilute acids and heat, di- and polysaccharids are hydrolyzed. The hydrolysis of a few of the important saccharids is given:

	Enzymes.	Products.
Sucrose	sucrase or invertase	{ Equal parts of glucose and fructose (invert sugar).
Maltose	maltase	{ Two molecules of glucose.
Lactose	lactase	{ Equal parts of glucose and galactose.
Starch Glycogen	amylases (ptyalin diastase, etc.)	{ Dextrins and maltose.

Raffinose is hydrolyzed by strong mineral acids to a molecule each of glucose, fructose, and galactose. Inulin



is easily changed by acid hydrolysis to fructose; it is not ordinarily attacked by enzymes. Cellulose and starch are considered anhydrides of glucose, and both yield glucose on acid hydrolysis. Ordinary cellulose is not, however, hydrolyzed by amylases or other enzymes, but by bacterial action.

The hydrolysis of pectic bodies is complex, and the cleavage products not definitely known. A substance is found associated with cellulose in the cell walls of unripe fruits to which the name pectose is given. As the fruit ripens, pectose is converted by enzyme action into pectin. This change can be brought about by boiling pectose with dilute acids or caustic alkalis, and the products include not only pectin in several forms but a number of acids. Pectin has the power of swelling in water and gelatinizing, a property of which advantage is taken in jelly making. (See Chap. VIII.)

In household practice many examples of hydrolysis occur, *e. g.*, when starch and sugar are cooked with fruit acids; in the process of caramelizing sugar or in making fondant. Sugar hydrolyzes much more quickly than starch.

**Optical Activity.**—Nearly all carbohydrates are optically active. Pure sucrose has a right rotation of  $66^\circ$ ; its hydrolytic products, glucose and fructose, show mutarotation, but the average figure for dextro-glucose is  $+52.5^\circ$ , that for fructose or levulose is  $-93.8^\circ$ . Since the pull of fructose to the left is greater by  $41.3^\circ$  than that of glucose to the right, it can be seen that an equal

mixture of the two would have a left rotation, opposite to that of sucrose. For this reason the name invert sugar is given to the hydrolytic products of sucrose. A practical application of this is made in the use of the saccharimeter (q. v.), by means of which the purity of cane sugar is determined by estimating the amount of invert it may contain.

**Solubility.**—The mono- and disaccharids are soluble in water. Of the polysaccharids, starch is not soluble in cold water, but in hot water the granules burst and the contents become a gelatinous mass known as starch paste. Dextrin is soluble in cold water, more readily in hot; glycogen dissolves with an opalescent appearance; cellulose is not soluble in either hot or cold water. In strong alcohol the monosaccharids are sparingly soluble; of the disaccharids maltose dissolves most readily, sucrose to a limited extent, lactose is almost insoluble. All the polysaccharids are insoluble.

**General Reactions.**—*Molisch's Test.*—All carbohydrates respond to Molisch's reagent. To about 3 cc. of a dilute solution of any carbohydrate add 2 or 3 drops of Molisch's reagent, mix thoroughly, and carefully pour concentrated  $\text{H}_2\text{SO}_4$  down the inclined side of the test tube. A violet ring appears at the contact surface of the liquids.

*Furfural.*—All carbohydrates yield some furfural on treatment with boiling  $\text{HCl}$ ; the pentoses are distinguished by the formation of large amounts.

**Ultimate Composition.**—I. *Determination of Hydrogen and Oxygen Evolved as Water.*—Heat about 1 gram of granulated

sugar in a clean dry test tube. Observe the condensation of moisture in the cooler part of the tube.

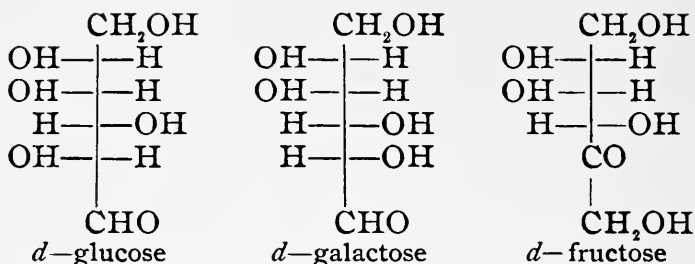
2. *Determination of Carbon.*—(a) By dehydration. Treat about 1 gram of the sugar in a porcelain evaporating dish with a little concentrated sulphuric acid, heat gently and note the blackening effect. In this case, the concentrated sulphuric acid withdraws the hydrogen and oxygen in the form of water and leaves the carbon. (b) By direct heat; continue heating (Experiment 1) and note the blackening of the mass due to freeing of some of the carbon.

3. *Determination of Hydrogen and Carbon in the Form of Hydrocarbons, i. e., Tarry Bodies.*—Observe the pungent odor of the vapors arising from the tube during the heating in experiment 2 (b). These usually condense on the cooler part of the tube in the form of a dark brown liquid (caramel).

### Glucose.

**Preparation.**—Glucose is prepared commercially in the United States by hydrolysing starch with dilute hydrochloric acid under pressure, neutralizing with soda ash, and evaporating the product in vacuum pans. It is sold in syrup and in crystal form. Commercial glucose contains varying amounts of dextrin. By carrying the hydrolytic action further, pure glucose or grape sugar may be produced.

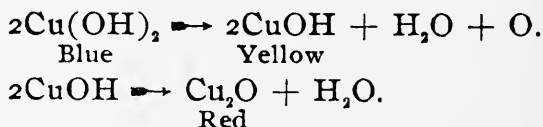
**Constitutional Structure.**—That glucose is an aldohexose is proved by its reactions. The structural formula usually assigned to it is  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHO}$ . The space configuration shown on next page illustrates the isomeric differences between glucose and the other important hexoses:



**Properties.**—Glucose is crystalline, soluble and diffusable. It crystallizes with difficulty from water, more readily from alcohol. In the first case the crystals appear as thin plates in amorphous masses, usually containing water of crystallization. Anhydrous needle or prism crystals may be obtained from alcohol.

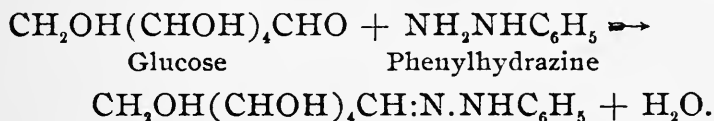
Nearly all yeasts readily ferment glucose, producing for the most part alcohol and carbon dioxide:  $\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{CO}_2 + 2\text{C}_2\text{H}_5\text{OH}$ .

**Reducing Power.**—Glucose shows its aldehyde character in its power of reducing metallic solutions such as are found in Fehling's, Barfoed's or Nylander's reagents, or alkaline silver nitrate. In the last a deposit of silver is formed; in Fehling's and Barfoed's the reduction from a higher to a lower copper oxide is shown by a color change from blue to red. Fehling's solution is the one most commonly used to determine the presence of a reducing sugar. The reactions taking place in changing from the cupric hydroxide to the cuprous oxide may be briefly indicated as follows:

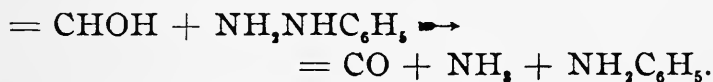


The reduction of Fehling's by glucose may be made quantitative, 50 milligrams of glucose reducing 10 cc. of the standard solution.

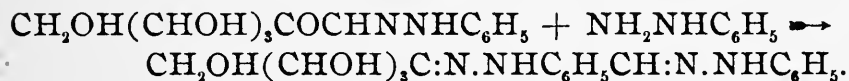
**Formation of Osazone.**—With phenylhydrazine glucose forms yellow needle crystals of phenylglucosazone, which are an identification test for this sugar. The change involves several reactions, in the first of which a hydrazone is formed:



A second reaction takes place, more phenylhydrazine acting as an oxidizing agent on the adjacent =CHOH group:



The CO left forms a second hydrazone group with phenylhydrazine present, the product being called an osazone, in this case phenylglucosazone:



**Action of Acids and Alkalies.**—When boiled with strong HCl, glucose is oxidized to levulinic acid,  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH}$ ; with nitric, to saccharic acid  $\text{COOH}(\text{CHOH})_4\text{COOH}$ . If heated with strong caustic soda or potash a series of complex reactions of an oxidative nature take place, and a brown color results. All carbohydrates with a free carbonyl group give this reaction.

**EXPERIMENTS ON GLUCOSE.**

1. Taste, and note the sweetness. (Glucose is about three-fifths as sweet as cane sugar.) Roughly determine its solubility in hot and cold water and in alcohol. Does it react with iodine?

2. **Effect of Heat.**—Heat some dry glucose in a clean dry test tube, note the result.

3. **Effect of Strong Acid.**—To some dry glucose in a porcelain dish add cold concentrated sulphuric acid: note the result. After allowing the test to stand for 5 minutes, heat gently and again note the result.

4. **Effect of Strong Alkali.**—To some glucose solution add strong caustic soda or potash and heat; note the result.

5. **Crystallization.**—Make a syrupy solution of glucose and allow it to stand for several days. Do any crystals form?

6. **Fermentation.**—Combine equal portions of compressed yeast with solutions of glucose, lactose, maltose and sucrose of equal strength, and starch paste. Fill the long arm of five bulb fermentation tubes with the five mixtures and close the bulb with a cotton plug. Stand in a warm place until fermentation begins. In each case note the rapidity with which carbon dioxide rises in the long arm of the tube and presses the liquid into the bulb, and draw conclusions as to the comparative action of yeast on the four sugars and the starch. Examine the liquid in the bulb for alcohol by (1) taste, and (2) heating with a small amount of iodine and sodium carbonate solution.

7. **Fehling's Solution Test.**—In a 100 cc. flask take 5 cc. of copper sulphate solution and 5 cc. of alkaline Rochelle salt, mix and add 20 cc. of distilled water, cover with a watch crystal and boil for 2 minutes. No change should take place. Add a few drops of glucose solution, boil vigorously for 2 minutes, cool and note the result. Continue adding glucose and boiling until on cooling the blue color of the solution has faded and a red precipitate is formed.

NOTE: The solution under test must be neutralized if acid,

as acids destroy the necessary alkaline condition of Fehling's and act in some degree as reducing agents.

**8. Barfoed's Solution.**—Add a few drops of glucose solution to a small amount of Barfoed's in a test tube, place the tube in boiling water for a few moments. A clear red precipitate appearing around the edges of the liquid indicates reduction to cuprous oxide. Barfoed's is an acid preparation—the test solution added to it must not be alkaline.

**9. Silver Mirror Test.**—To illustrate the reducing action of glucose on silver nitrate make a silver mirror as follows: Clean the article to be silvered—either a watch crystal or a small test tube—with nitric acid, water, and strong alcohol in the order mentioned, and place in contact with hot water. Make a strong solution of glucose. Take sufficient 5 per cent.  $\text{AgNO}_3$  to fill the article, add ammonia cautiously until the precipitate formed almost disappears on shaking, then 1 or 2 cc. of the glucose solution. Mix quickly and fill the glass receptacle. When the reduction to metallic silver seems complete, pour off the solution.

**10. Preparation of Phenylglucosazone.**—To 0.2 gram of pure glucose dissolved in 4 cc. of water, add 0.4 gram of phenylhydrazine hydrochloride, and 0.6 gram of crystallized sodium acetate. Filter the solution if not clear, close the test tube with a cotton plug, warm in a water bath until yellow crystals of phenylglucosazone appear. Observe these under a microscope.

**Glucosides.**—These are complex substances found in the vegetable kingdom, which on hydrolysis yield a carbohydrate—generally glucose—and one or more other compounds. Many glucosides are known, together with the hydrolyzing enzymes which usually accompany them in the plant. A well known example is amygdalin, found in bitter almonds, and the kernels of peaches, cherries, plums, etc. It is hydrolyzed by the emulsin of almonds to glucose, benzaldehyde, and hydrocyanic acid. Phlor-

idzin is found in the root bark of apple, pear, plum and cherry trees, and yields glucose and phloretin by acid hydrolysis.

### Fructose.

The occurrence of fructose or levulose in nature has been given, also its space configuration (p. 96). The term *d*-fructose does not indicate the direction of its rotation of polarized light, which is left-handed, but its derivation from *d*-glucose. *L*-fructose turns polarized light to the right, being the mirror image of *d*-fructose.

Fructose is harder to crystallize than glucose, but forms fine rhombic needles. It is somewhat sweeter than cane sugar.

**Reactions.**—1. Resorcin gives a characteristic color reaction with fructose, due to the ketohexose nature of the latter. Carbohydrates such as cane sugar which yield fructose on hydrolysis, also give this reaction.

Mix equal volumes of hydrochloric acid and fructose solution and add a few drops of resorcin solution. Warm; notice a deep red color and the formation of a brownish precipitate.

2. Substances which, like fructose, have a ketone radical linked to a  $=\text{CHOH}$  group, act as reducing agents in alkaline solutions such as Fehling's.

3. Milk of lime precipitates fructose as an insoluble calcium compound, and thus can be used to separate the constituents of invert sugar, since the glucose remains in solution.

### EXPERIMENT.

Dissolve 50 grams of pure honey in 250 cc. of water, cool



with ice, and add 30 grams of slaked lime in small quantities, stirring constantly. Filter off the precipitate, wash it with a little water, press strongly to remove excess liquid, suspend it in water and pass a stream of carbon dioxide through the mixture. The lime compound of fructose is decomposed. What precipitates? Filter, and evaporate the fructose in the filtrate to a syrup. Test with Fehling's and resorcin.

If invert sugar is used for the above experiment decrease the amount to  $\frac{1}{5}$ .

4. With phenylhydrazine fructose gives an osazone identical with phenylglucosazone.

Fructose may be obtained by extracting inulin from dahlia tubers and hydrolyzing it.

#### EXPERIMENT.

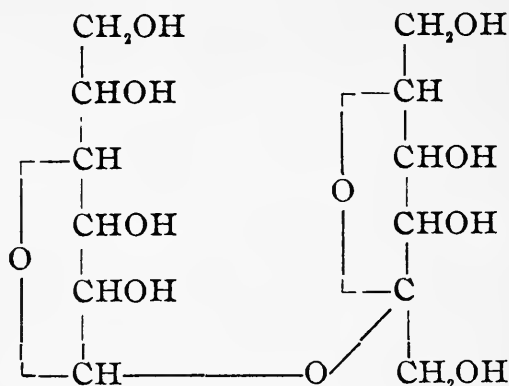
Grate several dahlia tubers, suspend the gratings in water, filter through muslin, collect the inulin as it settles at the bottom and mix with water. Heat this aqueous mixture on a water bath for an hour, with a few drops of  $\text{H}_2\text{SO}_4$  as the hydrolyzing agent. Neutralize with barium hydroxide, filter, and evaporate the filtrate at low heat to a syrup. Apply tests given above for fructose.

#### Galactose.

Galactose is an aldose, which is not found in the free state, but can be prepared by hydrolyzing lactose and separating the products, glucose and galactose, by crystallization of the latter from aqueous alcohol. It crystallizes in prisms which melt at  $168^\circ$ . Galactose is mutarotatory, with an equilibrium value of  $+81^\circ$ . With phenylhydrazine it forms a compound similar to glucose. Galactose is fermentable, but not by ordinary yeast.

### Sucrose.

Sucrose is an alcohol, with no free aldehyde or ketone group, as is shown by its formula:



It therefore does not act as a reducing agent when pure. Chemically, it is identical whether produced from cane, beets, or maple sap. It crystallizes easily into large octohedrons, and is the most readily soluble in water of all the carbohydrates. In strong alcohol it is scarcely soluble. Sucrose hydrolyzes readily with acids and even with heat alone. In the latter case the product is called caramel, and the beginning of the inversion corresponds with the first yellowing of the sugar.

**Saccharimeter Test.**—The purity of cane sugar, *i. e.*, its freedom from invert, is determined by a modification of the polariscope called a saccharimeter. In one type of the instrument, using the Ventzke scale, the light passes through the polarizer, from that through the tube containing the sugar solution, and then through the analyzer. This is a pair of quartz wedges arranged to neutralize

the rotating effect of the sugar, and at the same time record the degree of rotation on a scale. The rotating effect of pure sugar,  $+ 66^{\circ}$ , is read as 100 per cent. on the scale; a reading of less than 100 per cent. indicates impurity, and the amount of invert present can be calculated.

For the saccharimeter test (using the Ventzke scale) 26 grams of cane sugar are dissolved in the least quantity of water and made up to 100 cc. The solution must be clear and colorless. In case it is not, the color may be discharged by means of a solution of basic acetate of lead, which precipitates dextrin and gummy matter, and by bone-black, which removes soluble coloring matter. The operation is conducted as follows: 26 grams of sugar are dissolved in somewhat less than 100 cc. water, a few cc. (not more than five) of the lead solution are added and the solution diluted to mark. The mixture is shaken vigorously and then allowed to stand for a few minutes for the bulky precipitate to settle. If perfectly clear and colorless, the liquid is poured into the tube; if the color has not entirely been removed a subsequent treatment with alumina cream is necessary. For this purpose not more than 5 cc. of freshly prepared alumina cream are added to the liquid, the mixture is well shaken and allowed to stand for the precipitate to settle. The mixture is then filtered through dry paper, the first 10 cc. of the filtrate being rejected. It may be necessary to refilter through the same paper two or three times. The tube of the instrument is then filled with the solution,

the rotating effect determined, and the percentage of purity read on the scale.

### EXPERIMENTS ON SUCROSE.

1. Roughly determine its solubility in cold and hot water, and in alcohol. Is the solubility affected by heat?

2. **Crystallization.**—Make a hot syrupy solution of sugar and suspend in it a piece of glass rod by a thread. Set aside and allow to cool and after a time carefully examine the crystals of cane sugar.

3. **Effect of Dry Heat.**—Boil down sugar solution to dryness and note the result.

4. **Effect of Strong Acid.**—Drop some concentrated sulphuric acid on dry sugar, note the result and compare with starch and glucose.

5. Boil weak sugar solution with Fehling's solution. If pure there should be no reduction.

6. **Hydrolysis.**—"Inversion."—Boil sugar solution with a few drops of concentrated hydrochloric acid, cool, neutralize with sodium carbonate and heat again with Fehling's solution; note the result and compare with glucose. What change has taken place?

7. Test hydrolyzed and unhydrolyzed sugar solution with Barfoed's.

8. **Effect of Strong Alkali.**—To 10 cc. of sugar solution add some strong caustic soda, heat and note the result; compare with glucose.

9. **Specific Test.**—To 15 cc. of the clear liquid, add 5 cc. of cobalt chloride (5 per cent.) and 2 cc. of caustic soda (50 per cent.). Sucrose gives an amethyst-violet, permanent on heating. Glucose gives a turquoise-blue, turning to green on standing some time, or on gentle heating. This test may be used on condensed milk, honey, preserves, etc.

10. **Caramel Test.**—Boil a strong solution of sugar until it has turned brown (caramel), cool, dilute and test some of the liquid with Fehling's solution.

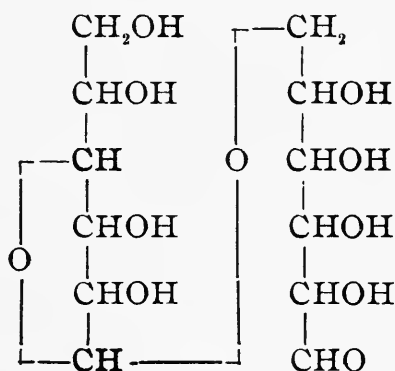
11. **Saccharimeter Test.**—Determine the purity of samples of cane sugar by the saccharimeter.

12. **Formation of Sucrosate.**—Sucrose unites with metallic hydroxides such as calcium and barium to form sucrosates. Calcium sucrosate may be prepared by saturating lime water with cane sugar at low heat. The product is commonly called viscogen, and is used as a thickener in whipping cream, etc.

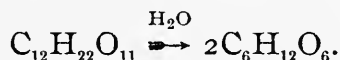
13. **Resorcin Test.**—To a solution of cane-sugar add an equal volume of HCl and a few crystals of resorcin. Warm. A deep red color appears, due to the formation of fructose.

### Maltose.

Maltose does not occur in nature, but is produced during the hydrolysis of starch by unorganized ferments, such as ptyalin and diastase. It is an aldose, as is shown by its formula:



On hydrolysis maltose yields two molecules of glucose:



Maltose is readily soluble in water and crystallizes from it in fine plates in the hydrated form  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$ . It becomes anhydrous by drying at  $100^\circ$ . In the hydrated state it dissolves more freely in alcohol than do

sucrose and lactose, and in this way also can be separated from its mixture with most dextrans, which are precipitated by alcohol of over 60 per cent. strength.

With phenylhydrazine, yellow crystals of phenylmaltosazone form which resemble irregular daisy petals or knife blades.

The maltase in ordinary brewer's yeast acts readily on maltose, hydrolyzing it to glucose.

It requires 80 milligrams of maltose to reduce Fehling's, against 50 milligrams of glucose.

#### EXPERIMENTS ON MALTOSE.

**Preparation of Diastase in the Form of Malt.**—Malt is produced during the germination of barley and other cereals. Prepare it as follows: Spread out a thin layer of barley grains (one tablespoonful) on the cover of a small pasteboard box, moisten with warm water and keep in a moderately warm place. Each grain will soon begin to sprout. When the rootlet has grown the length of the grain, dry it in an oven at a low temperature and keep bottled. Make malt extract by grinding the grains coarsely and extracting them with 100 cc. of warm water. Note the taste and odor of the liquid. Keep for future use.

**Preparation of Pure Maltose.**—Make a thin paste of starch and boiling water, cool to 65° and add 10 cc. of malt extract, prepared as above, and continue the heating at 65° for half an hour. From time to time test small portions of the liquid with iodine solution. When the liquid fails to react blue, cool the balance of the solution divide in 6 parts and test as follows:

1. **Solubility in Alcohol.**—Add some of the liquid to strong alcohol, allow to stand and note the white precipitate of dextrin: the liquid contains maltose.

2. **Effect of Fehling's Solution.**—To 10 cc. of Fehling's solution add a few drops of the liquid, boil for 2 minutes and note the

reduction; add more of the solution and boil again; repeat until the reduction is complete.

3. Test with Barfoed's reagent.

4. Apply the fermentation test.

5. Test with strong caustic soda or potash.

6. Repeat the phenylhydrazine test. Compare with glucose.

NOTE.—The above tests may be made on commercially prepared maltose.

### Lactose.

Lactose, or milk sugar, is a disaccharid containing a free carbonyl group. The structural formula for maltose (q. v.) may be used to represent lactose also. It is a reducing agent, 67.8 milligrams being required to reduce completely 10 cc. of Fehling's.

Lactose is less soluble in water than sucrose or maltose. Five or six parts of cold water are required for solution, or about two and one-half parts of boiling water. When crystallized from water at low temperature it contains one molecule of water of crystallization, which is lost by heating the crystals to 130°. Lactose is insoluble in alcohol.

With phenylhydrazine yellow crystals of phenyl-lactosazone are formed, which resemble chestnut burrs. Ordinary yeast does not ferment lactose, but lactic ferments convert it into lactic acid and alcohol. It readily undergoes butyric acid fermentation also.

Lactose is hydrolyzed by lactase or by dilute mineral acids to a molecule each of glucose and galactose.

### EXPERIMENTS ON LACTOSE.

**Preparation.**—Allow milk to stand until well soured; filter. Faintly acidulate the whey with dilute acetic acid and heat to

coagulate protein material. Filter, and evaporate the filtrate over hot water to crystallization. The crystals are crude lactose.

Take some of the lactose so prepared, or the commercial form, and make the following tests:

1. Note the hardness and slightly sweet taste, due to the limited solubility.
2. Try its solubility in water and in alcohol.
3. Treat some dry powdered lactose with concentrated sulphuric acid, note the result.
4. Try the caustic soda reaction.
5. Apply the Fehling's test.
6. Test with Barfoed's reagent.
7. Make a weak solution of lactose in water, let it stand at least 24 hours in a moderately warm place, and then test for acidity.
8. Make the phenylhydrazine test, compare with glucose and maltose.

### Starch.

Starch is the most widely distributed carbohydrate. It is found in varying proportions in leaves, stems, woody tissues, roots, tubers, fruits and seeds, but is especially abundant in the cereal grains and in tubers such as the potato. The formula  $n(\text{C}_6\text{H}_{10}\text{O}_5)$  is used to express its large and complex molecule, but soluble starch—or its principal constituent, amylo-dextrin—is sometimes represented as  $(\text{C}_{12}\text{H}_{20}\text{O}_{10})_{54}$ .

**Physical State.**—Pure starch is a white, powdery substance, colloidal and granular. The granules are definite in average size and appearance according to their source. Potato starch has one of the largest granules. They are ovoid in shape, and show concentric layers which increase in thickness with their distance from the nucleus



or hilum. The size increases with age. The outer layer of starch granules is known as starch cellulose; the contents as granulose or amylose.

**Effect of Heat.**—In hot water the outer layer of starch granules is ruptured and the contents gelatinize, forming a partial solution known as starch paste. The temperature of gelatinization varies from  $65^{\circ}$  to  $85^{\circ}$ , according to the kind of starch. Root and tuber starches gelatinize at a lower temperature, as a rule, than cereal starches. According to some investigators<sup>1</sup> gelatinization is caused by a mucilaginous substance, amylo-pectin, found in the granule. This body does not give the iodine reaction, and swells without dissolving in hot water.

Ordinary air-dried starch is dextrinized at temperatures from  $160^{\circ}$  to  $210^{\circ}$ . Reducing sugars may possibly be formed. With higher temperatures, and out of contact with air, starch yields products similar to those formed in the dry distillation of wood.

**Effect of Low Temperature.**—On cooling, starch paste contracts. Its greatest contraction is at freezing point, when a permanent separation of water and starch takes place to a considerable extent, and the starch dries out as a powdery mass. This substance is often noticed on starched clothes dried after being frozen, and such clothes have lost most of their stiffness.

**Soluble Starch.**—Starch is manufactured in several grades with regard to thickening quality. With long

<sup>1</sup> Maquenne and Roux: *Ann. Chim. Phys.*, 1906 [8], 9, 179.

Matthews and Lott: *J. Inst. Brewing*, 1911, 17, 219-266.

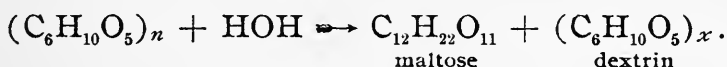
continued heating or heating under pressure at  $130^{\circ}$ - $150^{\circ}$ , with ten times its weight of water, a form of starch is prepared which goes into true solution. It does not gelatinize, but gives the iodine reaction and does not reduce Fehling's.

**Reaction with Iodine.**—This is the most characteristic test for starch. A deep blue color is produced whether the granule is ruptured or not. The compound formed is called starch iodide.

**Action of Acids and Alkalies.**—On boiling with dilute (2 per cent.)  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , starch is hydrolyzed to dextrins and maltose, and finally to glucose. Concentrated  $\text{H}_2\text{SO}_4$  causes a complete carbonization of air-dry starch in a short time. Strong  $\text{HCl}$  on dry starch causes a swelling of the granules and in a short time a change to the soluble form. If the action is continued for a few days, hydrolysis of the granules to achroodextrin, maltose and glucose results, while the starch cellulose remains unchanged. With nitric acid various products are formed according to conditions. On boiling with strong  $\text{HNO}_3$  (specific gravity 1.2) starch is converted into oxalic acid. With cold concentrated  $\text{HNO}_3$  compounds may be formed similar to the nitrates of cellulose. In presence of cold strong fixed alkali, starch is soluble with partial hydrolysis and usually the product has a distinct yellow color; weaker solutions have very little effect unless heated.

**Action of Enzymes.**—Amylases, whether the diastase of grains, the ptyalin of the saliva, or the amylopsin of

the pancreatic secretion, hydrolyze starch to maltose. The first reaction is a quick change of starch paste to soluble starch. Shortly after, the blue color with iodine gives place to a reddish brown, showing the presence of erythrodextrin. At the same time maltose is formed. The change may be expressed as :



As the action continues an achroodextrin stage is reached where the iodine ceases to act, and the amount of reducing sugar is increased. According to Maquenne and Roux, the maltose is produced from the principal constituent of the granule, amylose, and the residual dextrin comes from the amylo-pectin, which is slowly changed by enzyme action, but does not yield a reducing sugar. Experiments by these investigators and others show about 80 per cent. of maltose formed after 2 hours of diastatic action. Hydrolysis with diastase proceeds most rapidly at a temperature of about 55°.

**Fermentation.**—Various organisms are known which ferment starch to alcohol. With yeast there is no direct fermentation; if a diastatic enzyme is present in the starch hydrolysis to maltose may take place, in which case the maltase in ordinary yeast carries the hydrolysis to glucose. This in turn is converted by zymase to various substances, chiefly carbon dioxide and alcohol.

### EXPERIMENTS ON STARCH.

1. **Occurrence of Starch.**—Examine a thin section of potato under the microscope. Make a careful drawing of the structure of the cells and the granules within. Cover the section with a

thin glass and introduce a minute trace of iodine solution at the edge of the cover glass. Note and make a colored (blue pencil) diagram of the result.

2. **Extraction of Starch.**—Clean and peel one end of a small potato, rub it on an ordinary grater, collect the gratings in a beaker of cold water, strain, allow the cloudy liquid to stand until starch settles. Pour off liquid and use the sediment for following tests:

3. **Effect of Dry Heat.**—Gently heat half an inch of dry starch in a clean, dry test-tube. Observe and explain condensed moisture in the cooler part of the tube. Increase the heat somewhat and note the odor of the evolved vapor and the color of the starch: What does it suggest? Now heat strongly until only a black residue remains. What is it?

4. **Effect of Strong Acid.**—To a small portion of dry starch in a porcelain evaporating dish add a few drops of concentrated sulphuric acid; note the result and after a short time heat gently and observe again.

5. **Solubility.**—Treat a small portion of finely pulverized dry starch with cold water, filter a portion and examine the filtrate for dissolved material, by evaporating a little on platinum foil, also by the iodine test.

6. **Starch Paste.**—Boil the remainder of the starch and water mixture. Filter some of the gelatinized product and test a portion of the filtrate with iodine. Explain.

7. **Conditions for Iodine Tests.**—To another portion of the cooled filtrate add iodine solution, gently heat and allow to cool. Note the result. Now boil for some time and cool; the color will not return. Why?

To some starch solution in a test tube add a small portion of caustic soda and a few drops of iodine solution and note the result. Repeat the experiment using dilute sulphuric acid instead of NaOH.

8. **Effect of Tannic Acid.**—Add a solution of tannic acid to some starch solution. Note the result, also any change effected by heating.

9. **Starch a Colloidal Substance.**—Partly fill a diffusion thimble with thin starch paste, then stand it in a beaker of cold water. After standing for some time, test the water for starch with iodine.

10. **Acid Hydrolysis.**—1.—Make a very weak solution of starch in about 4 ounces of boiling water; to this solution add 2 cc. of strong hydrochloric acid and boil until clear, using a reflux condenser. At this point, a small quantity of the cooled liquid should give no blue coloration with iodine solution. If this is not the case add 10 drops of the same acid and boil some minutes longer, or until a small portion gives no test with iodine as above. Now neutralize the remainder of the liquid with sodium carbonate solution, add 1 or 2 cc. to Fehling's solution and boil. If reduction does not take place add more of the solution and boil again.

2. Mix about 1 gram of starch with 10 cc. of strong HCl and allow the mixture to stand for 15 minutes. Now pour off a small portion and add an excess of cold water. A milky precipitate of soluble starch results. Filter this and test its solubility in hot water. Allow the remainder of the acid mixture to stand for several days, until the viscous mass becomes clear and separates into 2 layers. The upper layer contains starch cellulose. Remove and test with iodine. Neutralize the lower layer and make the Fehling's test.

**Enzyme Hydrolysis.**—1.—Take about 25 cc. of clear dilute starch paste in a small beaker and add 2 or 3 cc. of undiluted saliva which has been filtered through coarse filter paper.

Keep at body temperature and from time to time pour off small portions and test with iodine solution, keeping each for comparison. Note the gradual change from blue to red to yellow and finally to colorless. When this stage is reached, add a small portion of the material to Fehling's solution, boil, and note reduction due to maltose.

2. To 25 cc. of dilute starch paste add about 5 cc. of diastase solution and keep at 55°. Test portions from time to time with iodine until the test fails to give a color (maltose). At this stage boil the remainder of the solution with about 25 drops of dilute sulphuric acid for 10 minutes. Neutralize and test this with Fehling's solution for glucose.

### Dextrin.

The dextrins are colloidal compounds, soluble in water, and precipitated by strong alcohol. As starch hydrolysis proceeds a number of dextrins are formed: the dextrin which gives a red-brown color with iodine is termed erythrodextrin; that which is forming as iodine ceases to act is achroodextrin. A maltodextrin is known to which the formula  $6(C_6H_{10}O_5)H_2O$  has been assigned. It appears to be a chemical combination of one part maltose and two parts dextrin, and is a reducing substance. Dextrins proper are not considered to have reducing power when pure.

Dextrins are used to a great extent in textile and other industries for sizings, as a medium for colors in textile printing, as gum, paste, etc. They also form about half the carbohydrate material in corn syrup.

**Preparation.**—Dextrin or "British Gum" is prepared commercially by two methods: (1) Dry starch is heated to 200°-250° over an oil bath, in a steam jacket, or other device to insure the requisite temperature without charring. The product is dark in color, but has good adhesive quality. (2) The starch is moistened with nitric or hydrochloric acid, dried, and heated to 140°-170°. The result of this partial hydrolysis is a light colored dextrin

containing some sugar, and having, therefore, less adhesive power. Dextrin may be prepared more conveniently by heating a strong starch paste with moderately dilute sulphuric acid until clear, cooling and precipitating by adding to ethyl alcohol.

### EXPERIMENTS ON DEXTRIN.

**Solubility.**—Compare the solubility of dextrin in cold water and in boiling water.

To successive portions of cooled dextrin solution in test tubes add:

1. Alcohol up to 60 per cent. by volume.
2. Iodine solution.
3. Caustic soda and iodine solutions.
4. Sulphuric acid and iodine solutions.
5. A few drops of ammonia and basic acetate of lead; note the result.
6. To boiling Fehling's solution: if pure there will be no reaction.
7. Tannic acid as under starch.
8. For the hydrolysis of dextrin by enzyme action, follow the method given under starch.

### Glycogen.

Glycogen is known as animal starch, since it appears as the reserve carbohydrate in the developing cells of animal organisms. It is present in the liver in considerable quantity; to a less extent in blood, muscle and several glands. Its formula is  $(C_6H_{10}O_5)_n$ . In appearance glycogen is a white, amorphous powder. It is soluble to opalescence in water, insoluble in strong alcohol, and hydrolyzes as starch does with diastase or with acids. It gives a brownish red color with iodine, does not re-

duce Fehling's, and is not fermentable by yeast. It may be extracted in considerable quantity from the large muscle of the scallop, as directed below:

**Preparation.**—Grind a mixture of scallops and sand in a mortar, transfer to a beaker, add enough water to cover the mass and boil. This dissolves the glycogen and partially precipitates the proteins, which are now completely precipitated by partially cooling and adding a few drops of acetic acid. Filter and add the filtrate to alcohol (95 per cent.). Glycogen will come down as a white precipitate. Allow to settle, decant the clear liquid, and filter the residue.

Apply the following tests to the glycogen thus obtained:

1. Solubility in water; look for opalescence.
2. Solubility in 10 per cent. sodium chloride solution.
3. Solubility in hydrochloric acid.
4. Solubility in caustic potash.
5. Reaction with iodine solution.
6. Boil a dilute solution of glycogen in a beaker for 15 minutes with 2 cc. of dilute hydrochloric acid, neutralize with sodium carbonate and test with Fehling's solution. What change has taken place?

### Celluloses.

These compounds, represented by the general formula  $nC_6H_{10}O_5$ , are at once the most complicated and stable of the carbohydrates.

They may be roughly divided into the simple and compound celluloses, the former unicellular in structure and the latter multicellular.

Cotton, thistledown, and the internal fibrous network



of grains and vegetables are simple celluloses and occur as ribbon-like bands with curled edges and a characteristic corkscrew twist. These forms contain little protein, gum, fat or mineral matter. Flax, grasses and woody fiber are compound celluloses, occurring for the most part as jointed rods or tubes, and are highly charged with protein, fat, gum and mineral matter. Cotton is the only unicellular form of cellulose of industrial importance, while the multicellular type has many representatives, *i. e.*, linen, hemp, jute, ramie and a great variety of woods.

The treatment of cotton does not involve any extensive chemical operations, but is chiefly confined to mechanical manipulation. The compound celluloses on the other hand require complex and prolonged chemical or bacterial treatment before the fiber is ready for the operations of spinning, weaving and dyeing. Woody fiber is now generally used for the preparation of the felted fabric known as paper. It is necessary in this case to remove all impurities by chemical means, and to break up the long fibers by grinding before the fabric can be prepared.

**General Properties of the Celluloses.**—Celluloses are insoluble in water hot or cold, and in weak acids or alkalies. Strong acids and alkalies cause them to hydrolyze; in some cases soluble forms result by heating or prolonged action in the cold, or by a combination of both methods. Generally speaking, the action of acids is more rapid. When partially hydrolyzed they are colored blue

in the presence of iodine. Nitric acid in concentrated form converts cellulose into nitric compounds of varying composition, containing one to six nitrate groups; the form depending on the duration of the nitrating process. All of these compounds are very unstable and dissociate into water, carbon dioxide and nitrogen, when slightly heated; hence their use as explosives. Cellulose nitrates, unlike cellulose, dissolve in ether, alcohol or acetone or mixtures of these solvents (collodion) and on evaporation yield transparent structureless films, used in medicine, photography and for the preparation of artificial silk. Ammoniacal cupric oxide (Schweitzer's Reagent) and concentrated zinc chloride dissolve simple cellulose on gentle warming. Hydrocellulose precipitates from these solutions on acidifying with acetic acid.

Lignocellulose (wood) yields oxalic acid on treatment with nitric acid, and oxalate of potash on fusion with caustic potash.

Cellulose fibers are characterized by high capillary capacity and heat conductivity; hence their use for lamp wicks, toweling and summer clothing. These properties, however, may be much modified by tight twisting and close weaving, as in the case of canvas.

While ordinary cellulose is considered an anhydride of glucose, and hydrolyzes to glucose, a hemi-cellulose is known which yields mannose, galactose, arabinose and xylose on hydrolysis, but no glucose.

#### EXPERIMENTS ON CELLULOSE.

(a) **Effect of Heat (Charring).**—Heat a piece of fibrous material in a clean dry test-tube. Note the odor of the gases

evolved and test the vapor with blue litmus paper. Examine the charred mass with a magnifier.

(b) **Solubility in Water.**—Try to dissolve some fibrous material in water.

(c) **Solubility in Zinc Chloride.**—Dissolve some absorbent cotton in acid zinc chloride solution, ( $\text{ZnCl}_2$  dissolved in twice its weight of concentrated  $\text{HCl}$ ). Precipitate by dilution and compare the result with the original substance.

(d) **Solubility in Schweitzer's Reagent.**—Dissolve some absorbent cotton in Schweitzer's reagent, add the resulting solution to 95 per cent. alcohol and compare the precipitate with the original substance.

(e) **Structure.**—Examine carefully the structure of cotton and linen fibers under a microscope.

(f) **Crude Fiber.**—Crude cellulose of wood, grains, etc., is determined as follows:

Take 1 gram of the dried, ground sample, boil with 100 cc. of  $1\frac{1}{4}$  per cent. sulphuric acid, when cool strain through muslin. Wash once with hot water. Scrape the residue from the muslin and boil it with 100 cc. of  $1\frac{1}{4}$  per cent. caustic soda. Strain again through the same piece of muslin, wash with hot water, then with alcohol, and finally with ether. Weigh the dried residue.

**Nitrating.**—Treat a piece of filter paper or some absorbent cotton with a cooled mixture of 20 cc. concentrated  $\text{H}_2\text{SO}_4$  and 10 cc. concentrated  $\text{HNO}_3$ . Keep the solution cool. Several nitrates of cellulose may form. The hexa- and penta-nitrates are the most prominent. The hexa-nitrate of cellulose is called gun cotton. Wash the product in water and dry. Test its inflammability, and its solubility in a mixture of 40 per cent. alcohol and 60 per cent. ether. The clear solution is collodion. Observe how a film of it hardens in the air. When pressed through capillary tubes, filaments are produced, which are denitrated and further treated to form one class of artificial silk—the nitro-cellulose or pyroxylin.

**Mercerization.**—Stretch some cheesecloth or muslin tightly over a porcelain dish and immerse for 15 minutes in a 25 per cent. solution of caustic soda, at a temperature of about 20°. An alkali-cellulose forms, and the cloth appears semi-transparent. Wash free from alkali, dry, and notice the appearance of the mercerized cotton compared with the original material. Try its reaction with iodine. The cotton has become cellulose hydrate,  $n(\text{C}_6\text{H}_{10}\text{O}_5)\text{H}_2\text{O}$ .

**Methods of Distinguishing Cotton from Linen.**—The microscope is the one reliable means of differentiating these fibers, since full-bleached linen and cotton are practically identical in chemical composition. However, the following tests are helpful if a microscope is not available:

**Breaking and Burning Tests.**—Unraveled threads of linen fabrics are untwisted and broken by holding between the thumbs and index fingers and pulling apart slowly and steadily. Linen parts slowly, and with pointed ends; cotton breaks suddenly with tasselled ends. Burn a small tuft of each fiber and note the condition of the fiber ends.

**Sulphuric Acid Test.**—Place a piece of union toweling in concentrated  $\text{H}_2\text{SO}_4$  for about  $1\frac{1}{2}$  minutes. Remove, wash, and note the comparative strength of the cotton and linen threads. Cotton will be destroyed in 2 minutes or less; linen as a rule not so quickly.

#### TESTS ON LIGNOCELLULOSE.

(a) **Structure.**—Examine carefully the character of the fibers, *e. g.*, hemp or jute.

(b) **Phloroglucinol Test.**—Phloroglucinol, in  $\text{HCl}$ , gives a deep magenta coloration with any of the lignocelluloses.

The reagent is prepared by dissolving the phenol to saturation in  $\text{HCl}$  (1.06 specific gravity).

(c) Saturate moist jute fiber, held in a glass tube, with chlorine gas and then pass  $\text{SO}_2$  through it. Note the characteristic reaction, a deep magenta color.

### TESTS ON PAPER.

Determine starch as filler with iodine solution. Determine "size" by moistening the paper with Millon's reagent and warming gently.

**Parchment Paper.**—Dip starch-free paper in a cold mixture of water and  $\text{H}_2\text{SO}_4$  (2:3), withdraw quickly, wash in clear water and dry. Compare with an untreated sample. Make the iodine test. (Cellulose in the presence of certain dehydrating agents responds to iodine.)

### Practical Work on Carbohydrates.

#### I. EXAMINATION OF CEREALS.

**Materials.**—Ready-to-eat cereals of different types—flaked, and shredded. Uncooked cereals—rolled and granular.

**Method:** 1. Grind samples fine in mortar. Make cold water solution. Filter. Examine filtrate as follows:

- a. For soluble starch (iodine).
- b. For dextrin. Add carefully to 95 per cent. alcohol. Note precipitate. Continue adding the filtrate, observing whether the precipitate decreases in amount. If so, the alcohol has been diluted below 60 per cent., and dextrin has gone into solution. Starch remains insoluble. If much dextrin is present iodine will show it.
- c. For reducing sugar. Make Fehling's and Barfoed's tests.
- d. For protein. Make biuret test (see p. 148).

2. Stain a portion of the residue with iodine and examine under the microscope for unbroken starch granules.

3. In a muffle furnace, burn to ash about 5 grams of oats, rice, etc. Take up the ash with boiling water and a few drops of  $\text{HNO}_3$ . Filter, cool and test for Fe, Ca, Mg, K, Na, P and Cl.

#### II. COOKING OF CEREALS.

Cook different cereals for the minimum time stated on the package. Observe condition of granules under microscope.

(Note that a ruptured granule does not always lose its form or contents.) Observe again after a longer cooking.

### III. PREPARED SOUPS.

Treat prepared dried puree soups as in II and observe.

### IV. CRACKERS, BREAD, TOAST, ETC.

Examine as in I for unchanged and changed starch, dextrin and reducing sugar. Compare under microscope stained slides of bread from crust and center of loaf.

### V. POTATOES.

Bake and boil until cooked. Examine under microscope. Make salivary digestion test on well-cooked potato, examining under the microscope the condition of the granules in the dextrin and maltose stages.

### VI. HYDROLYTIC CHANGES.

Test sugars for reducing action after boiling with cream of tartar (fondant making), lemon juice, or other acid fruit juice. Note time required for hydrolysis and the completeness of the change. Make similar tests on starch and compare with sugar as to quickness of action.

### VII. HONEY AND SYRUPS.

Test for cane and invert sugars.

### VIII. THICKENING POWER.

Note comparative thickening power of potato, corn, and wheat starches, and time required for cooking.

**Preparation of Gluten.**—Take 25 grams of white bread, macaroni or whole wheat flours, mix on a porcelain or glass plate with the least amount of water to make a stiff dough (12-15 cc.). Do not handle the dough with the fingers, use a flexible steel knife. Transfer the dough to a well-washed piece of muslin, taking care to clean the

mixing surface and knife thoroughly; tie up the muslin in the form of a bag and wash under a gentle stream of water, manipulating well with the fingers. Continue the washing until the liquid runs clear from the bag, and fails to give the test for starch with iodine. Be careful to collect all the washings in a tall glass beaker or jar—they should amount to from 1 to  $1\frac{1}{2}$  liters). Strain through muslin and stand the filtrate aside in a cool place for settling. Reserve for future use. Examine the residue with a lens. Squeeze out as much water as possible from the bag, untie it and collect and weigh the moist gluten; spread it out in a thin cake and dry it for 1 hour at  $100^{\circ}$ - $105^{\circ}$ . Cool and weigh the dry gluten. When the contents of the jar have settled, decant the clear liquid, and test small portions of it for protein with the biuret test and for soluble carbohydrate with Fehling's reagent.

Pour distilled water on the residue in the jar and stir up the mixture, allow it to settle and decant as before. Repeat this operation twice, and then collect the residue on balanced filter papers; dry and weigh. This last weight gives the starch and fiber content, but in the case of ordinary wheat flours the latter is so small that it may be neglected.

NOTE.—In the case of a whole wheat flour it is best to pass the sample through a 100-mesh sieve, taking the screenings for the determination of starch, gluten, etc.

## CHAPTER VIII.

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### FRUITS AND FRUIT JUICES.

**Composition.**—Analyses of fresh fruits show similarities in composition, so that a general description is sufficient. The percentage of water is always high, being from 75 per cent. to more than 90 per cent. in the edible portion.\* The next highest constituent is the carbohydrate bodies.

*The carbohydrates* in ripe fruits are principally glucose and fructose. Starch and acids decrease as fruit ripens; invert increases. Sucrose normally disappears with the increase of invert. Many fruits, especially berries, contain little or no sucrose; in apples, pears, peaches, apricots, oranges, plums and pineapple the amount is comparatively high. Celluloses, forming the fiber content, are of course a considerable carbohydrate part of some fruits. Pectose is found combined as pectocellulose in the lamellae of cell walls. When hydrolyzed with dilute acids or alkalies, or by pectase, an enzyme present in ripening fruit, pectose changes to pectin. The former is insoluble in water, and may be decomposed into a number of substances known as pectinic acids, usually found combined with calcium. The term pectinase is applied to the enzyme which coag-

\* *Fruits and Fruit Products*, Bull. 66, U. S. Dept. Agric., Div. of Chem.

Bull. 28, Atwater and Bryant, *Idem*.



ulates the juices containing the dissolved pectinous substances, forming the so-called fruit jellies.\*

This reaction is conditioned on the presence of lime, and the establishment of a certain equilibrium between the enzyme and the concentration of the fruit acid and the calcium salts. Fleishy roots and fruits—carrots, turnips, apples and pears—are especially rich in pectocelluloses, but many other fruits, *e. g.*, currants, possess considerable amounts.

In unripe fruits there is often much tannin, which disappears as the fruit ripens.

*Acidity.*—The acidity of most fruits is due to mixtures of organic acids and acid salts, such as acid potassium tartrate. Citric, malic and tartaric acids are often present, and may be determined separately. However, for convenience, analysts usually express total acidity as sulphuric acid.

*Ash Constituents.*—In most cases, these show a marked alkalinity, and consist largely of carbonates of sodium, potassium, calcium, and magnesium. Sulphates and chlorides are found only in traces.

*Proteins.*—The protein content is inconsiderable, seldom reaching more than 1 per cent. in fresh fruit. Much of this is insoluble, and appears only in small quantities in the expressed juice. As a rule, the presence of more than 1 per cent. of protein in a jelly would indicate that gelatin had been used to aid in the gelatinizing of the article.

\* Kraemer: *Applied and Economic Botany*.

The following table from the *Ann. de Chimie et de Phys.*, Vol. 61, gives comparative figures as to content of reducing sugar, sucrose, total sugar and acid in various fruits:

	Per cent. of reducing sugar	Per cent. of sucrose	Per cent. of total sugar <sup>1</sup>	Per cent. of acid figured as tartaric <sup>2</sup>
Hot house grapes .....	17.26	0.00	18.37	0.345
Dried grapes.....	16.50	0.00	16.50	0.403
Dried pippins.....	12.63	3.20	15.83	0.403
Violet figs.....	11.55	0.00	11.55	0.057
English cherries.....	10.00	0.00	10.00	0.661
Fresh grapes .....	9.42	0.00	9.42	0.558
Fresh pippins.....	8.72	5.28	13.40	1.148
Dried pears .....	8.42	0.36	8.78	0.115
White heart cherries ....	8.25	0.00	8.25	0.608
Fresh pears.....	7.16	0.68	7.84	0.287
White currants .....	6.40	0.00	6.40	1.574
Strawberries.....	5.86	0.00	5.86	0.750
Dried apples.....	5.82	0.43	6.25	0.253
English pippins.....	5.45	2.19	7.64	0.633
Raspberries.....	5.22	2.01	7.23	1.580
Strawberries (different variety) .....	4.98	6.33	11.31	0.550
Oranges .....	4.36	4.22	8.58	0.448
Queen Claude plums ....	4.33	1.25	5.55	1.208
Mirabelle plums .....	3.43	5.24	8.67	1.288
Apricots ....	2.74	1.04	3.78	1.864
Pineapples .....	1.98	11.33	13.30	0.547
Green grapes .....	1.60	0.00	1.60	2.485
Peaches .....	1.07	0.92	1.99	0.783
Lemons .....	1.06	0.41	1.47	4.706

<sup>1</sup> Quoted by Buegnet.

<sup>2</sup> Quoted by König.

#### ANALYSIS OF A FRUIT.\*

Water and Total Solids.—Weigh out about 20 grams of the

\* Bull. 66, Div. of Chem, U. S. Dept. of Agric.

pulped fresh fruit, or about as much dried fruit as will give 3 or 4 grams of dried residue, place in a weighed flat dish, mix with a weighed quantity (4-5 grams) of freshly ignited asbestos, add a few cc. of water, mix thoroughly and dry at  $100^{\circ}$  for 20 to 24 hours. Estimate water and total solids.

**Determination of Ash.**—Thoroughly char the above residue in a platinum dish at as low a heat as possible, extract with water, filter, and wash. Return filter paper and insoluble material to the dish and thoroughly ignite; add the soluble portion and a few cc. of ammonium carbonate solution, and evaporate the whole to dryness. Now heat to very low redness, cool in a desiccator, and weigh rapidly. The result is total ash constituents.

**Determination of Alkalinity.**—Run an excess of  $N/5$   $HNO_3$  into the platinum dish containing the ash. Add a drop or two of methyl orange. Mix carefully with a rubber tipped stirring rod, and titrate excess of acid with  $N/10$   $KOH$ . Calculate alkalinity as potassium carbonate.

**Total Acids.**—Dilute 10 grams of fruit juice or pulped fruit up to 250 cc., with recently boiled distilled water. In the case of fruit pulp boil for a minute or two, to dissolve all acid from the fruit cells. Add phenolphthalein and titrate against  $N/10$   $KOH$ . Calculate as  $H_2SO_4$ .

**Scheme for the Separation and Identification of Malates, Citrates, Tartrates, Oxalates and Acetates.**—To the filtered fruit juice, prepared as in the preceding experiment, add  $Ca(OH)_2$ , preferably in the form of milk of lime, until the neutral point is reached. Avoid excess. (If the fruit juice is neutral at the start add  $CaCl_2$  solution as long as a precipitate forms.) Stir well, filter and wash. Proceed as follows with (1) residue; (2) filtrate:

1. Residue. (Containing calcium tartrate and oxalate).—Treat on a filter with acetic acid. Residue is calcium oxalate, soluble in hydrochloric acid. Filtrate contains calcium acetate and tartaric acid. Add 95 per cent. alcohol and potassium hydroxide, and shake well. On standing acid potassium tartrate appears as well-defined crystals.

2. Filtrate. (Containing calcium malate, citrate and acetate.)—Boil, filter, and wash with hot distilled water. Reserve filtrate. Residue is calcium citrate. Treat on filter with dilute sulphuric acid. Residue is calcium sulphate. To the solution add silver nitrate and dilute ammonia—a white precipitate of silver citrate forms which does not blacken on boiling. The reserved filtrate contains calcium malate and acetate. Concentrate, cool, and add to a large excess of ethyl alcohol. Filter and wash. Residue, calcium malate. Solution, calcium acetate. To this add sulphuric acid and heat. Note odor of ethyl acetate.

*Determination of Nitrogen.*—Use 5 grams of fruit jelly, or 10 grams of fresh juice or fruit. Follow the Kjeldahl method described in Chapter XVI. Use 6.25 as the nitrogen factor.

*Determination of Carbohydrates.*—(a) *Reducing Sugar.*—Treat 25 grams of fruit juice or pulp with basic lead acetate in excess (2 to 5 cc.), make up to 100 cc. and filter. Transfer from 25 to 50 cc.—depending upon the percentage of reducing sugar present—to a 100 cc. flask and add a saturated solution of sodium sulphate in sufficient amount to precipitate the excess of lead; complete the volume to 100 cc., filter, and determine reducing sugar by Allihn's method. (See Chapter XVI.)

(b) *Cane Sugar.*—When only a small amount of cane sugar is present, it is best determined by calculation from the increase in reducing sugars after inversion. Treat double the amount of fruit or juice used in (a) with basic lead acetate, make up to 100 cc., filter, and invert 50 cc. in a 100 cc. flask with 5 cc. of hydrochloric acid. (See Chapter XVI.) After inversion nearly neutralize the acid with sodium hydroxide, precipitate the excess of lead with sodium sulphate, and dilute with water to 100 cc. Filter and dilute so that the solution does not contain more than 1 per cent. of reducing sugar. The per cent. of increase in reducing sugar after inversion, multiplied by 0.95, equals the per cent. of cane sugar.

*Pentoses and Pentosans.*—*Furfural Test.*—Place 25 grams of the fruit juice, diluted to 100 cc., in an Erlenmeyer flask, add

HCl of 1.06 specific gravity and boil. Hold in the vapor a filter paper moistened with a solution of equal parts of anilin and 50 per cent. acetic acid. A bright red color appears on the paper if more than traces of furfural are present.\*

*Dextrin.*—A qualitative test may be made by decolorizing the diluted fruit juice with boneblack, and observing the color reaction with iodine. Another method of decolorizing consists in bringing the solution nearly to the boiling point, then adding several cubic centimeters of dilute (1 to 3) sulphuric acid and gradually potassium permanganate. Stir until the color disappears.

*Alcohol Precipitate.*—If alcohol is added in excess to a solution of a fruit product, such as a jelly, a flocculent precipitate may form with no turbidity, indicating a pure fruit product. A white turbidity appearing at once, followed by a thick, gummy precipitate, shows the presence of glucose. In fresh fruit juices there is often marked turbidity which is caused by the starchy matters present.

*Experiment in Jelly-Making.*—To determine the optimum conditions for gelatinizing fruit juices, treat cranberries, apples, currants, and other jelly-making fruits as follows:

1. Express the juice from the raw fruit and allow a portion to stand. Is there gelatinization in any case?
2. Bring another portion to a boil. Cool and observe.
3. Boil other portions for measured periods, increasing in duration. What is the relation of time to jelly formation?
4. Repeat (2) and (3), adding an equal bulk of sugar to the fruit juice at the boiling point.
5. Repeat (2), (3) and (4), modifying as follows:
  - (a) Heat the fruit until the skins burst, and express the juice.
  - (b) Boil the fruit for 5 minutes and express the juice.

*Isolation of Pectin.*—Grate fresh white turnips and extract all solubles with cool distilled water. Macerate the extracted residue with cold dilute HCl (1:15) for 48 hours, pour off the liquid and precipitate pectose bodies by adding an equal bulk of ethyl alcohol.

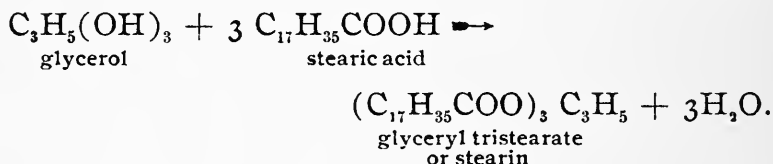
\* See Sherman: *Organic Analysis*.

## CHAPTER IX.

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### FATS.

Fats and oils are widely distributed in vegetable and animal forms of life. The line of distinction between a fat and an oil is not closely drawn, but fats are generally found as solids at about  $20^{\circ}$ ; oils as fluids. True fats and oils are esters, in which the base is always glycerol, although the fatty acids vary. They are therefore glycerides, the type formation of which is represented by the equation:



As found in nature, fats are not simple glycerides, but mixtures of two or more. For instance, from mutton and beef fat, a distearopalmitin, a dipalmitostearin and a dipalmito-olein have been separated.\*

The principal fatty acids represented in these mixed fats are:

\* Leathes: *The Fats*.

Saturated Acids.	Occurrence.
Butyric, $C_3H_7COOH$	Chiefly in butter.
Caproic, $C_5H_{11}COOH$	In butter (1.2%); in coconut and palm oils.
Caprylic, $C_7H_{15}COOH$	Same as caproic.
Capric, $C_9H_{19}COOH$	Same as caproic.
Lauric, $C_{11}H_{23}COOH$	Milk (trace); coconut and laurel oils.
Myristic, $C_{13}H_{27}COOH$	Milk (trace); lard, codliver oil, nutmeg butter.
Palmitic, $C_{15}H_{31}COOH$	In most animal and vegetable fats, <i>e. g.</i> , palm oil, butter, lard.
Stearic, $C_{17}H_{35}COOH$	In most fats, especially solid forms.
Unsaturated Acids.	
Oleic, $C_{17}H_{33}COOH$	In most fats and oils.
Linoleic, $C_{17}H_{31}COOH$	Linseed oil. This or a similar acid also in other vegetable oils, including cotton seed.

Since the fatty acids exist as liquids, semi-solids, and solids, the predominating acid or acids in a fat determine its character in this respect.

Chemically, the glycerides take their name from their fatty acid, combined with the suffix "in"—thus, stearin, palmitin, olein, etc.

**Properties of Fats.**—*Solubilities.*—With few exceptions, fats are practically insoluble in cold water and alcohol, sparingly soluble in hot alcohol; but dissolve readily in light hydrocarbons such as petroleum ether and gasoline. All fats are soluble in ether, chloroform, carbon tetrachloride and benzene.

*Odor and Taste.*—Pure neutral glycerides are nearly

all odorless and tasteless. An exception is butyrin, found in butter, which contains soluble butyric acid. The smell and taste of natural fats and oils are due to foreign substances, such as ethereal oils.

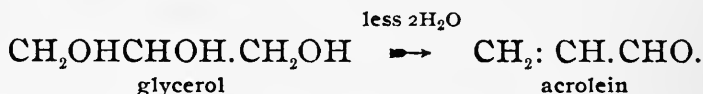
*Non-volatility.*—Fats and oils are non-volatile, therefore are called fixed, in contradistinction of ethereal oils. A result of this property is the formation of grease spots.

*Crystallinity.*—Fats are crystalline; the crystals of pure fats form a means of identification.

*Melting and Solidifying Points.*—In passing from the solid to the liquid state fats do not alter in composition. The melting and solidifying points of fats are definite unless the mixture is complicated. The solidifying points of oils range from a few degrees above zero to about  $-28^{\circ}$ .

*Specific Gravity.*—Most oils and fats have a specific gravity ranging from 0.910 to 0.975 at  $15.5^{\circ}$ .

*Effect of Heat.*—On prolonged heating in contact with air, or heated above  $250^{\circ}$ , fats and oils decompose, with formation of volatile products, notably acrolein. Acrolein is a decomposition product of glycerol:



It has a peculiar irritating odor characteristic of burning fat, and its formation is a simple means both of identifying the presence of a fat and distinguishing between a true fat or oil and a hydrocarbon oil.



*Emulsification.*—This is a physical change brought about by agitating a fat in the fluid state with some emulsifying agent such as egg albumin or soap solution. The fat is broken up into tiny globules which are coated with the tenacious medium and thus prevented from coalescing. Emulsions are more or less temporary, as in the case of mayonnaise, or the fat in freshly drawn milk, or permanent as in certain commercial preparations. Emulsification increases the area for chemical action in fat digestion.

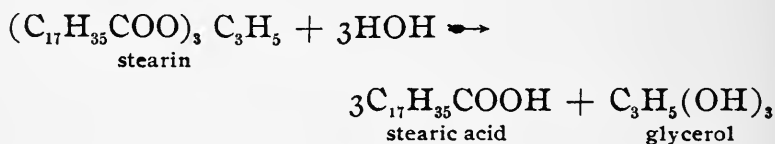
*Drying Oils.*—Three classes of oils are recognized: Non-drying, semi-drying, and drying. The distinctions are made according to their tendency to form a dry, elastic film on exposure to the air. The drying property in an oil is due to the presence of unsaturated fatty acids, which readily become saturated by combination with oxygen. Linseed oil is an example of an oil which quickly undergoes oxidation and is converted into a varnish. In this case drying is greatly hastened by a previous boiling of the oil.

*Iodine Value.*—The degree of unsaturation in a semi-drying or drying oil can be determined by the amount of iodine it will take up in the formation of addition products. This is known as the iodine number or value of the oil.

*Hydrogenation.*—By a process comparatively new, fats and oils containing unsaturated fatty acids are made to take up hydrogen by catalytic action and become sat-

urated compounds. Such fats are now being put on the market for edible purposes and for soap-making.

*Hydrolysis.*—The hydrolysis of fats, as well as of esters in general, is called saponification. The change is a splitting of the fat into its components—glycerol and fatty acids—illustrated by the reaction:

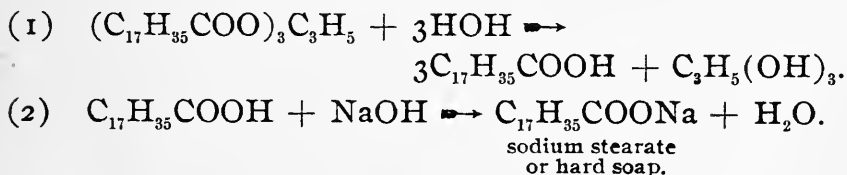


Moisture alone will not effect hydrolysis of fats in any definite length of time: a catalyst is necessary to accelerate the change. Heat, acids or alkalies, and enzymes act as catalytic agents. At a temperature of 200° or more, water, *e.g.*, superheated steam, attacks glycerides. If dilute HCl or H<sub>2</sub>SO<sub>4</sub> is used, the saponification occurs rapidly with less heat. Quick hydrolysis is also brought about by heating the fat with an excess of an alcoholic solution of caustic soda or potash. In this case the fatty acid set free unites with the alkali to form soap (see next page, and Chap. XV). If fat-splitting enzymes are present, hydrolysis may be brought about by moisture at normal temperatures. These enzymes occur in seeds containing vegetable oils, and during germination are active in changing the fat to a form utilizable by the embryo. As the quantity of enzymes in the filtered commercial oils is small, the per cent. of free fatty acid they contain is likewise small as a rule, and hydrolysis does not proceed if they are protected from air and moisture, or are not in contact with the organic material from

which they have been extracted. Under the reverse conditions the formation of free fatty acid may proceed to a considerable degree even in refined oils.

*Rancidity.*—Although a fat or oil may have an acid reaction, it is not necessarily rancid—the terms are not synonymous. Acidity precedes rancidity; the change to the latter state is supposed to be due to oxidation of free fatty acid by the oxygen of the air, in the presence of light. The peculiar taste of rancid fat is caused by these oxidation products. Bacterial action is not necessary to the change, for a sterile fat may become rancid, but the presence of foreign substances may favor enzyme or bacterial hydrolysis of the glycerides. Butter for this reason easily becomes rancid, as some protein material may be present.

*Soap-Making Property.*—Fats hydrolyzed with metallic hydroxides form soaps by the further action of the free fatty acid with the base. Using NaOH or KOH, the changes are:



If KOH is used, a soft or potash soap is made. With  $Ca(OH)_2$  an insoluble lime soap,  $(C_{17}H_{35}COO)_2Ca$ , is formed. This appears as an insoluble curd when soap is used in hard water. With  $PbO$  (or  $Pb(OH)_2$ ), a lead soap  $(C_{17}H_{35}COO)_2Pb$ , results. (See page 138, Exp. 9.)

**EXPERIMENTS ON FATS.**

**Ultimate Composition.**—*Hydrogen and Oxygen in the Form of Water.*—Boil 20-25 drops of clear olive oil in a clean dry test tube. Note the watery deposit in the cooler part of the tube; some of this running back will cause the fat to crackle.

*Glycerine.*—Continue heating the tube until dense fumes arise from the boiling liquid. This is due to acrolein,  $\text{CH}_2:\text{CH}.\text{CHO}$ , a decomposition product of glycerine. Note the odor.

Cool the tube and contents and reserve for next step.

*Carbon and Hydrogen as Hydrocarbons Resulting from the Breakdown of the Fatty Acids.*—Pour the cold tube contents into a clean dry porcelain dish and heat slowly but strongly over a low flame. Note the gradual darkening of the liquid due to freeing of carbon and the tarry coat on the rim of the dish (hydrocarbons). Hold a lighted match over the dish and note the inflammable character of the vapor (hydrocarbon gases). Extinguish the flame and continue the heating until only a black residue remains. This is carbon; prove it by burning off.

**Extraction of Pure Fat from Animal Sources.**—Weigh out 10 grams of beef suet cut up in small pieces. Place in a small evaporating dish and heat cautiously, so that no darkening of the fat occurs. (What causes the spattering?) When the spattering has ceased, strain through muslin into a porcelain dish, squeeze out the cloth and reserve the liquid for tests on fats.

Transfer the residue to a small mortar, add 5 cc. of strong alcohol, grind well. Pour this mixture into a small flask, wash out the mortar with alcohol and add the washings to the flask. Finally close the flask with a cork, bearing a condenser tube 24 inches long, support on a ring stand over a water-bath and boil for 10 minutes. When the suspended matter has settled, uncork the flask and pour the clear liquid on a small filter, allowing the filtrate to run into a large test tube. To the residue in the flask, add 20 cc. of ether, insert the cork and condenser and cautiously heat over hot water for 5 minutes. Then transfer

the entire contents of the flask to a small muslin filter and collect the filtrate in the same tube as before. Close the test tube with a loose cotton plug, allow it to stand until crystals deposit from the liquid. Examine these under the microscope and draw a diagram of them. Wash the residue from the last filtration with a little ether, squeeze out, spread on the muslin and dry. Take it up with a little water, add a few drops of Millon's reagent, and heat gently. A red color indicates protein matter.

Make the following tests on the rendered (extracted) fat:

1. Solubility.—Test the solubility of small portions of fat in separate test tubes with water hot and cold, alcohol hot and cold, and in hot  $\text{Na}_2\text{CO}_3$ , shaking the mixtures well. Record the results.

2. Absorption.—Place a small piece of fat on a filter paper and heat until the fat melts; note the result.

3. Formation of Acrolein.—Rub up a small piece of fat in a mortar with some acid potassium sulphate, transfer to a clean, dry test tube and heat cautiously; note the peculiar disagreeable odor of acrolein and the reducing effect of the aldehyde on a strip of filter paper moistened with ammoniacal silver nitrate.

4. Emulsification.—Shake together a few centimeters of cod-liver oil and dilute sodium carbonate. Notice the resulting white mass which is called an emulsion; what well known liquid is similar in appearance? Examine two or three drops of this emulsion under the microscope and note the character of the compound.

Repeat the experiment, using a few drops of olive oil and a solution of albumin.

5. Saponification with Alkali.—To about 1 gram of fat in a low flask fitted with a reflux condenser add 25 cc. of alcoholic potash solution, and boil. Replace the liquid lost by evaporation with alcohol. As the heating progresses, the mixture should become homogeneous; if it does not, add a little more potash and boil until clear (saponified). Remove the cover and evaporate the bulk of the alcohol, finally adding hot water and heating

until all alcoholic odor has disappeared. Cool the liquid, divide into three parts and use in (6) and (8).

6. Precipitation and Decomposition of Soap.—To one portion add a saturated solution of salt; notice the curdy precipitate (soap). Filter off this precipitate, try its solubility in cold water. Acidify another portion of the dissolved soap with dilute sulphuric acid. Note the curdy precipitate (fatty acids). Boil the mixture until clear, filter and use in test 7.

7. Test the solubility of the fatty acids in water, warm alcohol and sodium carbonate solution. Record results.

8. Formation of Lime Soap.—Add an excess of a solution of lime water to another portion of the soap solution and notice the greasy precipitate, which is insoluble in warm water and alcohol (lime soap, produced by hard water).

9. Formation of Lead Soap.—Heat a small quantity of lard or tallow for some time in an evaporating dish, with lead oxide,  $PbO$ , and a little water; filter off the watery liquid and evaporate a small quantity on a platinum foil. Note the characteristic odor of acrolein, proving the presence of glycerine.

10. Determination of Free Fatty Acid.—Take a weighed amount of olive oil (about 1 gram), add about 25 cc. of alcohol which has been neutralized with  $N/NaOH$  (one drop will probably be sufficient) and boil. While hot, titrate against  $N/10 NaOH$ . Calculate the percentage of fatty acid in the sample in terms of oleic acid.

11. Koettstorfer Number.—Weigh out 2.5 grams of fat in a low flask. Add 25 cc. of approximately  $N/4$  alcoholic potash solution, cover with a watch glass and heat on a water bath until the fat is completely saponified. Cool, and titrate back excess of alkali with  $N/2 HCl$ . Make a blank test in a similar manner on the alcoholic potash and calculate the per cent. of alkali absorbed in saponification. This test is used in the case of an unknown fat to determine its combining ratio with alkali.

12. Iodine Test.—Into each of two test tubes pour 20 drops of the oil under test. Dissolve the oil with about 5 cc. of chloroform. Add 4 or 5 drops of iodine solution to one of the samples;

cork and shake. To insure an excess of iodine, test by placing 1 drop of the mixture on filter paper. Observe the change in color in the tube to which iodine has been added, in case the oil contains unsaturated fatty acids.

13. Extraction of Fats from Cereals or Nuts.—Grind the sample to a fine powder and dry in an air bath at  $100^{\circ}$ - $105^{\circ}$  to constant weight. Weigh from 2 to 3 grams of the dried material, place in an extraction shell, and cover loosely with absorbent cotton. Extract in a Soxhlet apparatus with water-free ether for about 16 hours, allowing the extract to run into a weighed flask. Use a water-bath, or better, an electric plate, to avoid danger from overheating the ether. Finally evaporate the contents of the flask to constant weight and estimate the per cent. of fatty material removed in the ether extract.

14. Special Tests for Drying Oils.—(a) *Becchi's Test*.—To 5 cc. of the oil in a 6-inch test tube, add an equal volume of silver nitrate dissolved in alcohol (1 per cent. solution); close the test tube with a cotton plug and keep it in boiling water for 10 to 15 minutes. A darkening of the mixture indicates cotton-seed oil. The acids in cotton-seed oil quickly reduce the silver nitrate; those in olive oil only after some time.

(b) *Halphen's Test*.—To 5 cc. of the oil in a 6-inch test tube add 5 cc. of amyl alcohol and 5 cc. of carbon disulphide containing a little free sulphur. Close the test tube with a loose cotton plug and keep in hot water away from an open flame for  $\frac{1}{2}$  hour. A red coloration indicates cotton-seed oil. This is a very delicate test.

### BUTTER. SPECIFIC TESTS.

Wash a teaspoonful of butter in several waters until free from salt. Prove this by making the silver nitrate test on the last washing. Note any difference between the first and last washings when tested with litmus paper. Explain. Dry the washed butter between filter paper, melt, and dissolve in gasoline. Filter, and wash the residue on the paper with gasoline until a drop of the washings evaporated on paper leaves no greasy stain; dry

and note the character of the residue (curd). Cautiously heat this in a test tube with lime; observe the odor produced and hold in the fumes a piece of moistened red litmus paper and note the result.

**Spoon Test.**—Gently heat a piece of butter about the size of a cherry in a tablespoon. If it froths without spattering, it is pure butter. If it foams and spatters it is renovated butter; if it spatters only, it is oleomargarine.

**Butyric Acid Test.**—In a 4-ounce narrow neck flask, fitted with a one-holed rubber stopper, put about  $2\frac{1}{2}$  grams of butter. Saponify with caustic potash. Decompose the resulting product with dilute sulphuric acid in excess. Then distill the product gently, using a bent tube condenser. Butyric acid will distill at about the temperature of boiling water. Allow the distillate to drop into a funnel containing moist filter paper. This causes the retention of fatty acids (other than butyric). Below the funnel is placed an Erlenmeyer flask containing distilled water made alkaline by adding 2 drops of 10 per cent. NaOH, and tinted with phenolphthalein. The disappearance of the pink color will occur when sufficient butyric acid has passed over to neutralize the soda.



## CHAPTER X.

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### PROTEINS.

The proteins are the chief nitrogenous constituents of both plants and animals. Owing to their complex nature, the exact chemical structure of protein bodies has not been determined, but they are regarded as anhydrides of amino acids, since they yield these acids on hydrolysis.

The elementary composition of all proteins includes carbon, hydrogen, oxygen and nitrogen, with sulphur in typical forms. These elements are found in the following average ratio: Carbon 51-55 per cent., hydrogen 7 per cent., nitrogen 15-19 per cent., oxygen 20-30 per cent., sulphur 0.4-2.5 per cent. In addition, phosphorus is frequently found in direct or indirect combination with the protein molecule, and iron and calcium appear in some cases.

The large size of the protein molecule can be judged by the formula assigned to globin, one of the simplest forms:  $C_{726}H_{1174}N_{194}S_3O_{214}$ .

**Classification.**—Proteins are classified principally on the basis of differences in solubilities and hydrolysis. The classification which follows is the one recommended by the American Physiological Society and the American Society of Biological Chemists:

Proteins	{	Simple	{	Albumins
				Globulins
				Glutelins
				Alcohol
				Solubles
				Albuminoids
				Histones
				Protamines
	{	Conjugated	{	Nucleoproteins
				Glycoproteins
				Phosphoproteins
				Haemoglobins
				Lecithoproteins
	{	Derived	{	Primary derivatives
				Secondary derivatives
				Proteans
				Metaproteins
				Coagulated proteins
Non-proteins	{	Extractives	{	Proteoses
		Amides		Peptones
		Amino acids		Peptides

In this classification the group called *simple proteins* hydrolyze to amino acids, *conjugated proteins* yield protein decomposition products and some other body. This latter substance is nuclein in the nucleoproteins, a carbohydrate in the glycoproteins, a phospho body in the phosphoproteins, haematin in haemoglobins, and a fatty substance in lecithoproteins. The *derived proteins* are changed forms produced by the action of heat, acids or alkalies, or enzymes.

**Occurrence and Solubilities.**—*Albumins.*—In plant and animal bodies, as egg, plant, and serum albumin. Soluble in pure water, precipitated by complete saturation

with ammonium sulphate, but not by saturated magnesium sulphate or sodium chloride.

*Globulins*.—In animal bodies fibrinogen and derived fibrin, and myosinogen and derived myosin show globulin characteristics. Other forms are egg serum and lact-globulin. Examples in plants are legumin and edestin. Globulins are not soluble in water or in dilute acids, but dissolve in dilute solutions of inorganic salts. They are precipitated by saturation with magnesium sulphate or sodium chloride, or by half saturation with ammonium sulphate.

*Glutelins*.—Found in cereals; as glutenin in wheat and oryzenin in rice. Insoluble in all neutral solvents but readily soluble in very dilute acids and alkalies.

*Alcohol-Solubles* (Prolamines).—Gliadin (in wheat, combining with glutenin to form gluten in a dough mixture); zein (maize); hordein (barley). Insoluble in water and absolute alcohol, soluble in 70-80 per cent. alcohol.

*Albuminoids* (Scleroproteins).—Keratins of horn, hair, nails, egg membrane; collagen of white connective tissue, and elastin of yellow elastic tissue, yielding gelatin; silk gelatin and fibroin. Insoluble in all neutral solvents. Gelatin, a derived form, dissolves in hot water.

*Histones*.—Found combined with nucleic acid, forming certain nucleoproteins, *e. g.*, in the nuclei of blood corpuscles of birds, in the thymus gland, etc. Soluble in water, insoluble in very dilute  $\text{NH}_4\text{OH}$ .

*Protamines*.—Simple in composition; found in conjunction with nucleic acid in spermatozoa of certain fish. Soluble in water.

*Nucleoproteins*.—Widely distributed; form chief protein constituent of nuclei; contain nucleic acid combined generally with albumins, histones, or protamines.

*Glycoproteins*.—Ovo-mucoid; mucin of mucous membrane. Soluble in dilute alkalies; mucins reprecipitated by acetic acid, mucoids are not.

*Phosphoproteins*.—Caseinogen of milk, vitellin of egg yolk. Insoluble in water; readily soluble in alkalies, forming salts; precipitated by acids.

*Haemoglobins* (Chromoproteins).—Chromogenic substances, *e. g.*, haemoglobin in blood.

*Lecithoproteins* (Lipoproteins).—These are nitrogenous bodies combined with a fat radical. Examples are lecithans and phosphatides. Occur in yolk of egg, milk, etc.

*Proteans*.—Occur as insoluble products apparently resulting from the incipient action of water, very dilute acids, or enzymes.

*Metaproteins*.—Found in partial hydrolysis of proteins by the action of acids or alkalies; known as acid or alkali albumin or globulin, etc. Insoluble in water, soluble in dilute acids or alkalies, precipitated by alcohol.

*Coagulated Proteins*.—See *coagulation*.

*Proteoses*.—Intermediate products of protein digestion. Soluble in water, precipitated by alcohol or saturation with ammonium sulphate.

*Peptones*.—Further products of proteolysis. Soluble in water and saturated ammonium sulphate. Precipitated by alcohol.

*Peptids*.—Simple hydrolytic products of the protein molecule, which readily yield two or more amino acids on further hydrolysis. An example is glycyl-glycine  $\text{H}_2\text{N}.\text{CH}_2.\text{CO}.\text{NH}.\text{CH}_2.\text{COOH}$ .

*Extractives*.—Creatin and creatinin, found in muscle.

*Amides*.—Urea, asparagine in asparagus.

*Amino Acids*.—Simple decomposition products of the proteins.

**Properties.**—I. *General*.—Proteins are bodies of high molecular weight, optically active, colloidal, and generally colorless. Most proteins are amorphous, but some have been obtained in crystalline form, *e.g.*, edestin from hemp seed. They are both acid and basic in reaction.

2. *Coagulation*.—Many proteins, especially albumins and globulins, undergo a precipitation known as coagulation, on heating their aqueous solutions. The chemical change between the water and the protein is not clearly understood. Complete coagulation is only obtained in slightly acidified solution. Coagulated proteins are insoluble, and cannot be reconverted into the original protein substance. Different factors affect rapidity of coagulation, so that a range of temperature is usually given as the coagulation point of any specified protein. The hardening effect of alcohol on proteins is a form of coagulation.

3. *Curdling*.—This term describes a precipitation of protein material by acids or certain salt solutions, especially observed in the case of milk. The caseinogen in milk exists as a soluble calcium caseinogenate, which is broken up by the action of lactic or other acids and the caseinogen is thrown out of solution—*i. e.*, the milk has curdled. The calcium caseinogenate can be precipitated by salting out with sodium chloride.

4. *Clotting*.—Certain conjugated proteins undergo a change properly known as clotting, which occurs only through enzyme action. As seen in milk, the caseinogen is acted upon by rennin, which produces a soluble hydrolytic product, casein. The lime salt of casein is insoluble, and clotting can take place, therefore, only if soluble calcium salts are present to form the insoluble calcium caseinate. This is the clot produced in junket and cheddar cheese making. A similar change takes place in the clotting of the fibrinogen of blood, and, as far as is known, in the muscle tubes after death, causing rigor mortis.

5. *Hydrolysis*.—The hydrolysis of simple proteins yields the following as the principal decomposition products:

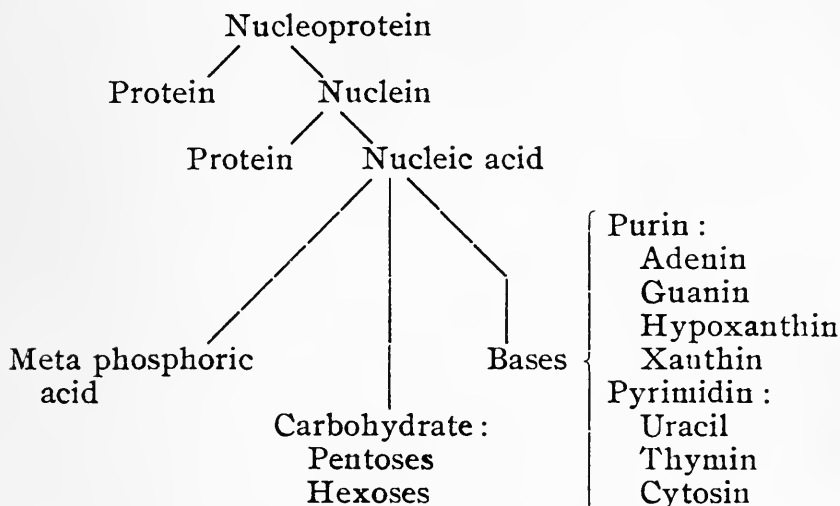
Protein  $\rightleftharpoons$  Metaprotein  $\rightleftharpoons$  Proteoses  $\rightleftharpoons$  Peptones  $\rightleftharpoons$  Peptides  $\rightleftharpoons$  Amino acids.

Most albumins and globulins also yield a carbohydrate substance, which in several cases, *e. g.*, egg globulin, has been identified as glucosamin.

Phosphoproteins split off an insoluble phosphorus

compound in the early stages of hydrolysis, which becomes soluble later in digestion. To this substance the names para- or pseudo-nuclein have sometimes been given.

Nucleoproteins hydrolyze as follows:



In the laboratory, complete hydrolysis may be effected by boiling with concentrated HCl for 6 to 12 hours, or with 25-33 per cent.  $\text{H}_2\text{SO}_4$  for 12 to 20 hours.

### TESTS ON PROTEINS

**Ultimate Composition.**—1. *Nitrogen as Ammonia.*—Mix some dried egg albumin with lime and moisten sufficiently to roll into small balls with the fingers. Place two or three of these balls in a dry test tube, heat and hold in the vapors a piece of moistened red litmus paper. Note the result. Let the paper dry and observe the change.

2. *Sulphur as Hydrogen Sulphide.*—Test the fumes with a piece of filter paper moistened with lead acetate and note the result.

3. *Hydrogen and Oxygen as Water*.—Observe the condensation of water in the cooler part of the tube.

4. *Carbon*.—Observe the blackening effect produced by the freeing of the carbon.

5. *Phosphorus*.—Place the well charred residue in a small portion dish, moisten with concentrated  $\text{HNO}_3$  and heat gently until excess of acid has been vaporized, then heat strongly until the carbon has been entirely consumed. Cool the residue, moisten with  $\text{HNO}_3$ , add water, boil and filter if necessary. Test the clear liquid with ammonium molybdate.

For the purpose of making general and specific tests on the proteins, a solution of egg albumin prepared according to the following directions is recommended.

**Preparation of Egg Albumin.**—Carefully break a fresh egg, allow the clear white to run into a porcelain dish and set the yolk aside for future use. Cut the white with scissors or grind with sand and place a small portion in a wide-mouthed stoppered bottle, add 10 volumes of distilled water, shake until it froths and invert over a small casserole of water. When the froth and insoluble protein particles float on the surface, carefully withdraw the cork and allow some of the liquid to mix with the water in the casserole. The liquid will probably be opalescent, due to traces of globulin; if strongly so filter through muslin, test the fluid with litmus paper and if alkaline neutralize with weak acetic acid (2 per cent.).

1. **General Tests.**—(a) *Nitric Acid* (Xanthoproteic reaction).—To a small portion of the filtered liquid, add strong nitric acid. This forms a white precipitate which turns yellow on heating; now cool and add ammonia—it becomes orange. Compare with spots on the skin or woolen cloth produced with  $\text{HNO}_3$ .

(b) *Biuret Test*.—To 1 inch of 10 per cent. caustic soda or potash, add dilute copper sulphate, drop by drop, until a faint blue color but no precipitate remains in the liquid after shaking; now add the protein solution. A violet color indicates protein; a pink, peptone.



(c) *Precipitation Tests*.—Solutions of the proteins are precipitated by the following reagents:

Alcohol.

Tannic acid.

Picric acid.

(d) *Coagulation by Heat*.—Heat some of the fluid to boiling and at the same time add, drop by drop, very dilute acetic acid (2 per cent.) as long as a precipitate forms; note that this precipitate does not appear unless the solution is acid. Attempt to filter some of the albumin through a wet filter paper; prove by one of the above tests that no protein is in the filtrate.

2. **Special Tests for Albumins and Globulins.**—(a) *Millon's*.—To a small portion of the solution, add Millon's reagent and heat. This forms a white precipitate which turns red on cooling, or gives a red color if only a trace of protein is present. Avoid using Millon's in the presence of sodium chloride.

(b) *Heller's Test*.—Place some strong nitric acid in a test tube and allow a solution of albumin to flow gently down the sides of the tube; a white ring of precipitated albumin forms at the junction.

(c) *Metaphosphoric Acid Test*.—Add a solution of albumin to a very little cold freshly prepared metaphosphoric acid and note the precipitate formed.

(d) *Adamkiewicz's Test*.—Add the protein solution to a mixture of 1 volume concentrated  $\text{H}_2\text{SO}_4$  and 2 volumes glacial acetic acid. Heat. A red violet color appears. Gelatin does not give this reaction.

(e) *Precipitation Tests*.—To portions of the solution in separate test tubes add:

Acetic acid and potassium ferrocyanide.

Mercuric chloride.

Lead acetate.

3. **Separation Tests.**—(a) To a portion of the solution, add an excess of dry crystallized ammonium sulphate, shake vigorously. Albumin and globulin will be precipitated, probably in a changed

form. Filter through a good grade of paper and make biuret test.

(b) To a portion of the solution, add dry sodium chloride or magnesium sulphate to saturation. Globulin is precipitated. Filter, and test filtrate with either nitric acid or Heller's test. This is a somewhat imperfect method of separating albumin and globulin.

4. **Indiffusibility.**—Place some of the solution in a dialyzer of parchment paper and suspend the whole in a beaker of distilled water. Test the water subsequently for chlorides with silver nitrate and also for protein by the biuret test.

5. **Proteolysis.**—(a) *Acid Metaprotein.*—To undiluted egg white add concentrated HCl; note the copious precipitate of albumin (coagulated). Heat gently until the mass dissolves resulting in a violet solution. Cool some of this liquid, testing separate portions as follows:

1. Heat to 70° by placing the test tube in hot water and raising the temperature gradually. Does any coagulation appear?

2. Neutralize with dilute caustic soda, filter and make the biuret test on the residue.

3. Add a few drops to 15-20 cc. saturated sodium chloride.

4. Add a few drops to 15-20 cc. 95 per cent. alcohol.

(b) *Alkali Metaprotein.*—Treat undiluted white of egg with strong alkali; note the clear jelly-like mass which results. Heat to clear solution and dilute some of this with water. Make the following tests:

1. Heat to 70°, as above.

2. Neutralize with dilute acetic acid, filter and make the biuret test on the residue.

3. Add a few drops to 15-20 cc. saturated sodium chloride.

4. Add a few drops to 15-20 cc. of 95 per cent. alcohol.

NOTE.—Weaker solutions of albumin are converted to metaprotein by treating with a few cubic centimeters of very weak alkali or acid (0.1 per cent.) at about 40° for some time.

**Proteose and Peptone.**—The action of pepsin is hydrolytic and produces both proteose and peptone—a case similar to the production of dextrin and glucose from starch. Make a pepsin digestion experiment as follows:

Coagulate egg albumin by heat. Cut into small wedge-shaped pieces, put into 3 test tubes and treat as follows:

1. Cover with highly dilute hydrochloric acid (0.2 per cent.).
2. Add a small amount of neutralized pepsin solution (0.1 per cent.).
3. Add a mixture of equal parts of pepsin and hydrochloric acid.

Place all 3 tubes in a beaker of cold water, heat to body temperature and note the time they take to clear; also observe whether the mass swells; finally filter all three and test the clear filtrates for peptone by the biuret test.

**Globulins.**—*Globulin from the White of Egg.*—Saturate some of the undiluted solution with dry magnesium sulphate, grinding the mass in a mortar. Observe the precipitate of globulin, filter and test the filtrate for protein. Now pour water through the insoluble mass on the filter and test the extract for proteins. Explain. The yield of globulins obtained from this source is very small and the following method is preferable:

*Globulin (Edestin) from Hemp Seed.*—Extract dry, ground hemp seed with sufficient 5 per cent. solution of sodium chloride to cover it well, first grinding the mass in a mortar, then heating it for about half an hour at 60°. Keep the mixture at this temperature and test as follows:

1. Filter a portion into a warm test tube, through a filter just previously washed with hot 5 per cent. NaCl. Notice the clearness of the filtrate. Cool under running water and observe the precipitate of crystallized edestin. Filter off a portion and observe the crystals under the microscope. Warm the remainder gently, and cool again. What happens?

2. Learn the solubilities of edestin by filtering a few drops of the clear solution as in (1) into (a) water, (b) alcohol, (c) saturated NaCl, (d) 5 per cent. NaCl (all at 60°).

3. Filter, and heat gently over hot water until coagulation appears. What is the coagulation temperature?

4. Make biuret and Heller's tests on the clear filtrate.

**Yolk of Egg.—Separation of Fat and Vitellin.**—Place one-half the yolk of a fresh egg in a broad 6-inch test tube, add twice its bulk of 95 per cent. alcohol, cork, shake vigorously, and place in water at 55° to 60°. When the mixture has separated into layers, decant the clear upper layer through a filter into a clean porcelain dish, and reserve for future use. Repeat with one or two further extractions until the residue in the tube is nearly white. Finally transfer it to a filter, wash with another portion of warm alcohol, and dry over warm water. The granular mass resulting is principally vitellin. Proceed as follows:

(1) *Fat*.—Evaporate the alcohol extract over hot water until no odor of alcohol remains. Note the yellow liquid oil. Take a portion and test for a fat. Add a few drops of  $\text{HNO}_3$  to the remainder and burn to ash; divide the ash in two portions and take up with a few drops of concentrated  $\text{HCl}$  and  $\text{HNO}_3$  respectively, add a little water to each and heat. Filter if necessary, test the  $\text{HCl}$  portion for *iron* with ammonium thiocyanate and the  $\text{HNO}_3$  portion for phosphoric acid with ammonium molybdate.

(2) *Vitellin*.—Mix thoroughly with 5 per cent.  $\text{NaCl}$  solution, keeping the mixture at 60° for 15 minutes. Filter a few drops into

(a) A large bulk of water made faintly acid with acetic acid.

(b) 95 per cent. alcohol.

(c) Saturated salt solution.

What are the solubilities of vitellin?

Heat another portion of the filtrate to coagulating point. What is it?

Make the nitric acid or Heller's test on another portion.

**Shell.**—I. Examine a portion of the shell under the low power of a microscope; note the physical character. Treat a portion of the shell with silicate of soda solution (10 per cent.); when

dry examine as before. (Silicate of soda is used for preserving eggs.)

2. Crush and grind the shell, thoroughly extract with warm water, dissolve the extracted mass with dilute hydrochloric acid. Note the effervescence. Hold in the fumes a drop of limewater on the end of a glass rod and note the clouding. What gas is formed? Filter the HCl solution and make slightly alkaline with ammonia, add ammonium oxalate and note the white precipitate of calcium oxalate, insoluble in acetic acid. From the data found give the composition of the shell and the changes which have taken place.

3. Allow an egg to stand in strong vinegar for several hours, remove, wash in one change of water, and note the peculiar condition of the egg. Examine the acid liquid as in the preceding experiment.

4. Examine equal portions of the yolk and the white of egg, separately, for sulphur by mixing with lime and testing with the lead acetate method given under proteins. Which do you think contains the greater amount of sulphur?

5. Weigh an egg accurately and repeat the weighing for five or six succeeding days. Record the results and explain.

For the average composition of the egg, see Sherman: *Food Products*.

### GELATIN.

By prolonged boiling with water gelatin is produced from collagen, which is a protein occurring in the connective tissue. The sources of both glue and gelatin are skin, bones, hoofs, hides, etc., but the latter should differ from glue both as to the condition of the raw material and the care used in the processes of manufacture.

### TESTS.

Place small pieces of gelatin in contact with cold water and note any change which takes place, then slowly heat the mixture

to boiling; does it coagulate? Cool a portion of the liquid; what happens? Test the remainder of the warm solution, divided into 10 parts, with:

1. Dilute hydrochloric acid.
2. Alcohol.
3. Acetic acid or lemon juice.
4. Picric acid.
5. Acetate of lead.
6. Salt and tannin.
7. Heller's test.
8. Biuret test.
9. Adamkiewicz's reaction.

10. Boil a water solution of gelatin for some time. Cool, and test its gelatinizing power. Gelatin is hydrolyzed by prolonged boiling, and will not gelatinize.

To estimate the quality of commercial gelatins, make the following tests:

1. The amount of ash should not exceed 2 per cent. Burn a weighed sample to ash of constant weight and estimate the amount.
2. Soak samples 4 hours, then make into a jelly by heating. Note odor: it should not be offensive. Expose a 5 per cent. solution to the air 2 days. Note odor.
3. Test gelatinizing power by comparing the firmness of jelly made by different samples under the same conditions.
4. Make comparative biuret tests. The color should be violet.
5. Make Millon's test. There should be little or no response.
6. Try litmus paper reaction. It should not be alkaline.

### BONES.

Bony tissue consists of a mixture of mineral matter (largely phosphate of lime) with protein (ossein). The

presence of both is easily shown by simple processes. If fresh bones be steeped for several days in 10 per cent. hydrochloric acid, the mineral matter will be removed and a shrunken but flexible cast will remain. On the other hand, the mineral matter of bone will persist after long careful heating in its original shape. The same result is accomplished much more slowly by weathering.

The food material in bone may be extracted as follows:

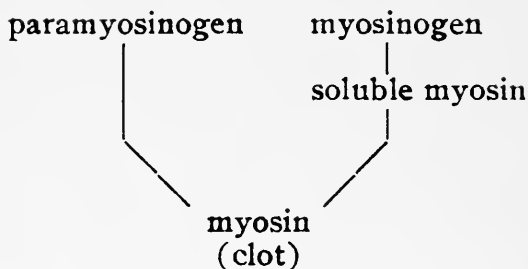
Procure raw shin bones of beef and have them well scraped and sawed into 1-inch sections. Treat these sections for 2 or 3 hours, under slight pressure, in a soup digester with the least possible amount of water. Pass the extract through cheese-cloth, filter into a tall glass cylinder, and when thoroughly cool, remove the layer of fat and compare with tallow.

Make tests for protein (biuret), and gelatin on the balance of the extract.

### MUSCLE.

The muscle mass consists of a series of elongated tubular sacks of yellow connective tissue (elastin) arranged in bundles and held together by white connective tissue (collagen). Interspersed in the mass are fat globules.

**Principal Constituents of Muscle.**—*Proteins.*—The total proteins of the muscle mass include serum albumin, serum globulin, haemoglobin, elastin, collagen, and especially paramyosinogen and myosinogen. These latter yield myosin on a clotting, as shown on next page:



The clotting action takes place at death. The globulin-like myosin is in turn gradually softened by acids set free by bacterial action (putrefaction) during “hanging”.

*Carbohydrate.*—Glycogen and glucose are generally present in muscle. They furnish energy for muscle contraction, yielding sarcolactic acid as one of the products of fatigue. Fresh muscle usually contains glycogen, but on standing this is rapidly changed to bacterial lactic acid.

*Extractives.*—These are certain nitrogenous non-protein bodies, principally creatin and creatinin. They give flavor to muscle, and being readily soluble, are found in meat extracts and soups.

*Mineral Salts.*—Principally potassium phosphate, also chlorides and other compounds of Ca, Fe, Na and Mg, including a trace of sulphates.

#### EXPERIMENTS ON MUSCLE.

Cut off the exterior of a piece of lean meat, test the interior with litmus paper and note the reaction. Then cut the meat in small pieces, pass through a meat chopper and grind the resulting mass in a mortar with clean, dry sand. Take one-half of the ground mass and extract in a beaker of cold water, stirring every few minutes. Allow the extraction to proceed for  $\frac{1}{2}$  hour. Finally filter off a part of the watery extract and test separate portions as follows:



1. Biuret.
2. Heat over water. At what point does coagulation begin?
3. Add crystals of ammonium sulphate to saturation; filter, and test precipitate and filtrate with biuret.
4. Determine whether glycogen is present as follows: Boil with a few drops of hydrochloric acid, neutralize, test with Fehling's.

Heat the remainder of the water extract to coagulate the protein and filter. To the filtrate add a few drops of  $\text{HNO}_3$  and burn to ash. Cool, take up with water, and if cloudy, filter. Divide into five parts and test for chlorides, sulphates, phosphates, calcium and iron.

Take the second portion of the ground meat, wash it free from blood, and extract it with three or four times its bulk of 10 per cent. sodium chloride, allowing it to stand 24 to 48 hours. Finally filter off the protein solution and test portions as follows:

1. Try reaction with litmus.
2. Pour a few drops into a large excess of water. Note milky precipitate of myosin.
3. Heat to coagulating point; what is it? Is the litmus reaction the same after heating?
4. Saturate with salt, shaking vigorously. What effect on the myosin? Filter. Dissolve precipitate in 10 per cent.  $\text{NaCl}$  and make biuret test on solution.

From the composition of muscle and the tests made deduce the effect on meat of washing, placing in dilute salt solution, corning, soup making, and roasting.

### BEEF EXTRACTS.

**Composition.**—The food value of these extracts is slight, and their function is to serve as stimulants or appetizers, and flavoring material. Commercial extracts

contain little if any protein material, since such proteins as may be extracted are coagulated by heat and removed by filtration. Home-made extracts and clear soups lose food value by clarifying. No fats or carbohydrates are found in the average market extract; the principal ingredients are extractives and the mineral salts of muscle.

#### TESTS ON HOME-MADE AND COMMERCIAL EXTRACTS.

Make meat extract by steeping lean meat in cold salt water, gradually heating to a boil and finally under slight pressure. Pour off the liquid, cool, remove the fat, dissolve some of the jelly in warm water and compare with Leibig's and other meat extracts made on the commercial scale, by the following tests:

1. Biuret.
2. Glycogen test (Iodine).
3. Creatinin (Weyl's Test).—Add a few drops of a 5 per cent. solution of sodium nitroprusside, freshly prepared, and cautiously 38° Baumé NaOH. A ruby red changing to straw color shows creatinin.
4. Examine the solid extract under the microscope and note the cubical crystals of salt and knife-rest forms of creatinin.
5. Clarify beef extract with white of egg, filter and test filtrate for protein with biuret. Compare with test on beef extract before clarifying.

#### MILK.

This term usually refers to cow's milk in market form. Analyses show that the composition of milk varies with different breeds of cows, the principal variation being in the fat content. Approximate averages are as follows.\*

\* For detailed composition of milk, see Sherman's *Food Products*.

	Per cent.	Per cent.
Water .....	87.2	87.0
Total solids .....	12.8	13.0
fat .....	3.6	4.0
protein .....	3.3	3.3
carbohydrate .....	4.9	5.0
ash .....	0.7	0.7

In most states, the amount of fat in milk offered for sale is regulated by law. The New York State Standard requires at least 3 per cent. fat.

**The Fats.**—The true fats in milk are glycerides of both volatile and non-volatile fatty acids. Of the former, butyric is the most important, forming 5 to 7 per cent of the fat content. When hydrolyzed, its free butyric acid gives a taste and odor to rancid butter. The principal fats of the non-volatile acids are palmitin in large amount, stearin, and olein. In freshly drawn milk tiny globules of fat are held in suspension by the mixed proteins present, but on standing the emulsion breaks, and the cream separates more or less completely. However, it is not until the emulsifying power of the protein is destroyed by the action of lactic acid developed in souring, that the fat particles run together and are combined in the form of butter by churning.

**Proteins.**—The protein constituents of milk are principally caseinogen, with small amounts of albumin, globulin, and fibrinogen. Caseinogen is strongly acid in character, is insoluble in water, but is held in solution

as a calcium-caseinogenate by the lime phosphates in the milk.

**Carbohydrate.**—Lactose is the main form of carbohydrate material. In amount it shows less variation than any other ingredient except mineral salts.

**Ash Constituents.**—The principal ash constituents are in the form of lime phosphates, found either combined with protein or other organic material, such as lecithin, or free as mineral salts. Combined citric acid is present in small amount, also chlorides and other salts of Na, K and Mg. Iron and sulphur are found.

**Other Constituents.**—Urea, creatinin, lecithin, cholesterol and hypoxanthine are present in varying amounts; also a color substance, carbohydrate- and fat-splitting enzymes, an oxydase, a reductase, and a catalase.

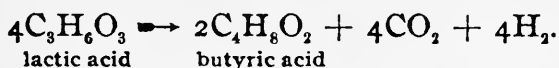
Fresh milk has an amphoteric reaction to litmus, due to the fact that it has two classes of phosphates in solution. Its specific gravity varies from 1.029 to 1.035.

**Effect of Heating.**—Under the conditions usually employed for pasteurization (145° F. for 1 hour) few if any chemical changes are produced in milk—the object being to destroy certain pathogenic bacteria. Boiling milk produces both physical and chemical changes, some of which are the alteration in the physical state of the fat globules, a tendency to precipitation of the lime salts, the destruction of most organisms, and the appearance of total solids in the skin which forms after boiling. This formation is not, as sometimes explained, coagulated protein material, but is due to the concentration of total solids as the water evaporates.

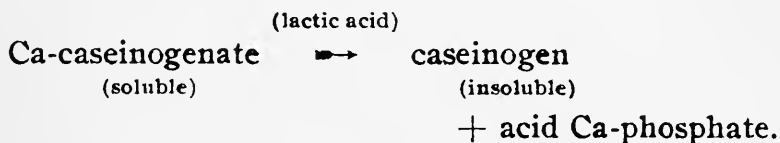
**Souring of Milk.**—By the activities of lactic acid bacteria lactose is decomposed into lactic acid:



Other fermentation products may also be formed, such as acetic, propionic or butyric acid, and some alcohol, *e. g.*:



When the lactic acid reaches approximately 0.5 per cent., caseinogen begins to be precipitated; the extreme amount of lactic acid developed is generally about 0.9 per cent. The action of acids on caseinogen has been described under *Curdling* (p. 146) but the changes taking place in this case may possibly be represented by the expression:



When baking soda is used with sour milk the acid caseinogen combines with the alkaline carbonate, forming sodium caseinogenate, carbon dioxide and water.

**Action of Rennin.**—The clotting action of rennin has been referred to under *Clotting* (p. 146). Conditions for the best action of the enzyme are brought out in experiments on p. 165.

**Fermentation with Yeast.**—Milk does not readily undergo fermentation with ordinary yeast unless some food for the yeast is added. For kephir or koumiss a special

yeast ferment is used, which changes the lactose into alcohol, lactic acid, and various other acid fermentation products.

### TESTS ON MILK.

**Physical.**—1. *Cream Gauge.*—Fill to mark with freshly mixed milk. Allow the tube and contents to rest quietly for half an hour and read off percentage of top milk from graduated scale.

2. *Lactometer.*—Fill a tall jar with freshly mixed milk, temperature 60° F. Immerse the instrument and when it comes to rest read off the percentage of purity on the scale. On the New York Board of Health lactometer the zero mark records a specific gravity of 1.000 and the 100 mark a specific gravity of 1.029. In similar manner, determine the purity of skim milk. Finally, add water and redetermine the purity; how can you explain the result?

3. *Pioscope Test.*—Depends on opacity. Place a drop or two of freshly mixed milk in the center of the hard rubber disc. Cover carefully with the glass plate and compare with the standard scale of colors.

4. *Lactoscope Test.*—Use Feser's lactoscope. Fill the pipette with milk, allow it to run into the cylinder. Cautiously add water, shaking after each addition, until the marks on the cloudy glass rod are just visible through the liquid. Read off and record the percentage of fat at the level of the liquid.

5. *Microscope Test.*—Examine a drop of milk under the microscope; add a drop of 10 per cent. caustic soda and re-examine. What is the result?

**Chemical Tests.**—1. Using fresh milk, what is the reaction with delicate litmus paper?

2. *Babcock Test (Determination of Fat).*—This test depends on the decomposition of the organic constituents, with the exception of the fats, which are at the same time set free in the liquid state and may be measured.

Fill the milk pipette (17.6 cc.) with freshly mixed milk, discharging the contents into the Babcock bottle, add an equal

volume of oil of vitriol (specific gravity 1.8). Mix by revolving the bottle gently in a small arc, back and forth, until the residue disappears and the mass is brown in color. Make tests up in duplicate and whirl them for 5 minutes in the centrifuge over hot water. Stop the machine, add enough warm water to bring liquid level half way up the graduated neck of bottle. Replace them in centrifuge and whirl 3 minutes, allowing machine to run down. Take out bottle and read per cent. of clear yellow fat floating on the water.

3. *Separation and Identification of Caseinogen.*—Dilute 10 cc. of fresh raw milk with water up to about 100 cc., add slowly the least quantity (6-8 cc.) of 2 per cent. acetic acid required to precipitate the caseinogen, warming meanwhile to  $60^{\circ}$ , filter through moist fluted paper and reserve the clear filtrate for test B. Operate with the residue as follows:

A. Residue of Caseinogen. Wash several times with the same amount of hot 95 per cent. alcohol, evaporate the alcohol extract over hot water, notice the appearance of the oily substance remaining, and make a fat test upon it. Remove excess of liquid from the caseinogen residue by pressing between dry filter paper, and spread out to dry. Dissolve a portion in about 25 cc. of warm 5 per cent. salt solution, slightly acidified with acetic acid. Stand in hot water for some minutes and filter. Add a few drops of the clear filtrate to a saturated solution of salt, adding dry salt if necessary. What are the solubilities of caseinogen in salt solutions? Make nitric acid and biuret tests on portions of the dissolved caseinogen. Add another considerable portion of the clear filtrate to ammonium oxalate, made strongly alkaline with  $\text{NH}_4\text{OH}$ . Heat and observe white crystalline precipitate of calcium oxalate. Fuse the remaining portion of dried caseinogen with sodium nitrate in a porcelain crucible, cool, and extract the contents of the crucible with diluted  $\text{HNO}_3$  (1:5). Filter, and add a few drops of the clear liquid to  $(\text{NH}_4)_2\text{MoO}_4$  solution. Warm and observe yellow crystalline precipitate, indicating presence of phosphoric acid.

B. Divide the whey filtrate (reserved) into three equal portions.

1. Heat in boiling water and observe the clouding (lactalbumin). Filter, test precipitate for protein, and filtrate for lactose with Fehling's reagent.

2. Add potassium ferrocyanide and excess of acetic acid. Observe the precipitate of lactalbumin.

3. Heat in boiling water, filter off lactalbumin, boil the filtrate and observe the precipitate, principally insoluble calcium citrate. Reserve filtrate.

NOTE.—If milk has been thoroughly pasteurized, it will not respond to the tests for lactalbumin.

C. Evaporate the filtrate, from last test, to dryness; ignite in the presence of a few drops of  $\text{HNO}_3$ , cool, dilute with water and test for chlorides, sulphates and phosphates.

**Analysis of Milk.**—Measure 5 cc. of milk with a pipette, transfer it to a weighed shallow porcelain dish and weigh again. Difference is weight of milk. Place over hot water (kept just below the boiling-point) to evaporate water present in milk. Cool and weigh; loss is water, residue is total solids. Total solids should be 12-13 per cent. To extract fat, add about 10 cc. of ether to contents of dish, heat over warm water 1 or 2 minutes, decant solution into a second weighed dish. Repeat the ether treatment three times. When dry, weigh original dish; the loss is fat. Evaporate ether from second dish, weigh; the gain is fat and should check the loss.

To extract lactose and soluble salts, treat contents of dish with warm water. Allow it to stand for several minutes, decant the liquid; repeat the operation three times. Dry the dish and weigh; loss is lactose and half the mineral salts found in milk.

Ignite the contents of dish to a gray ash; protein matter will burn off. Cool and weigh; the loss is protein, residue is insoluble salts. Assuming that insoluble salts are one-half of the total salts, double the figure obtained. To determine amount of lactose, subtract one-half of total salts from the figure obtained



on lactose and soluble salts. The difference is the amount of lactose.

**Determination of Lactose.**—Into a glass stoppered cylinder, put 100 cc. milk and 2 cc. Millon's reagent. Mix thoroughly and pour into a beaker placed over hot water. Allow the mixture to stand until all protein matter has precipitated, filter off the clear whey through moist fluted paper. Make it alkaline with dry sodium carbonate, adding a little at a time until pink litmus paper turns blue. If cloudy filter again. Pour into a burette and deal with it as with sugar. Calculate that 0.068 gram will reduce 10 cc. Fehling's reagent.

**Effect of Rennet.**—In the following experiments with rennet, make the tests comparative by using the same amount of milk and rennet solution throughout, *e.g.*, 10 drops of liquid rennet to 30 cc. of milk in each case.

1. Heat milk to the boiling-point, boil gently for 5 minutes, replacing any liquid lost during evaporation by hot distilled water, cool to 40° and add rennet; note the character and amount of clot.

2. Boil milk 15-20 minutes, keeping the liquid up to bulk as before; cool to 40°, add rennet; note character and amount of clot.

3. To the sample of milk, add 1-2 cc. of ammonium oxalate solution (precipitant for lime), boil for 2-3 minutes, cool to 40° and add rennet; note character and amount of clot, if any. Finally add limewater equal in bulk to the original milk, warm to 40° and note the result.

4. Repeat the above, adding 1 cc. of a dilute solution of calcium acid phosphate, instead of limewater.

5. Add 1 cc. of 0.2 per cent. HCl to the milk and test with rennet at 40°. Does a clot form? Repeat, using 1 cc. of 10 per cent.  $\text{Na}_2\text{CO}_3$ . What is the effect of alkali on rennet action?

6. Note the effect of rennet on separate portions of milk heated to 30°, 40°, 50°, 80°. Tabulate the results of the above tests.

**Butter-Fats.**—Half fill two small flasks (50 cc.), one with pure and the other with skim milk. Add to each half a volume of ether and a few drops of caustic soda, cork and rotate well. Uncork and place in a beaker of warm water and allow them to remain quiet. In a few minutes, note the layer of oil and ether floating on the surface. Remove some of the ether layer from each with a pipette and evaporate at a low heat. Note the differences in amount of the butter residue.

**Souring.**—1. Place some milk in a wide-mouthed bottle, allow it to stand in a warm place for some days or until sour. Finally filter off the curd and test the filtrate for lactose and for acidity by titrating with 10/N alkali, calculating to lactic acid. What weight of bicarbonate of soda would neutralize the amount of acid found?

2. Measure standard cupfuls of slightly sour, moderately sour, and very sour milk. Weigh the amount of baking soda required to fill a standard teaspoon and add the soda in small amounts to the milk sample, mixing thoroughly after each addition, and testing with litmus paper. Determine the weight of soda required to neutralize the acidity in each of the three samples of milk, and express the amount in fractional parts of a teaspoon.

**Condensed or Evaporated Milks** should be diluted with distilled water to the original bulk and treated as normal milks. The index of condensation may be estimated by observing the relative amount of dilution necessary.

Preserved milks commonly contain cane sugar. Dilute a sample to the original bulk, precipitate the caseinogen with dilute acetic acid; filter and exactly neutralize the filtrate with sodium carbonate and test for sucrose with cobalt chloride and caustic soda.

**Formalin in Milk.**—Add 1 drop of ferric chloride solution to 50 cc. of concentrated  $H_2SO_4$ . Pour 5 cc. of the mixture down the side of a test tube containing 20 cc. of the milk under test. If formalin is present, a violet band will appear at the contact point of the two liquids.

**Analysis of Ice Cream.—For Gelatin.**—Dilute 50 parts of ice cream with 25 parts of water and bring to the boiling point, to dissolve any thickener other than gelatin that may be present and not in complete solution. To 10 cc. of the product add an equal amount of acid nitrate of mercury solution<sup>1</sup> and about 20 cc. of cold water. Shake vigorously, allow to stand 5 minutes, then filter. If much gelatin is present the filtrate will be opalescent and cannot be obtained clear. To a portion of the filtrate add an equal volume of a saturated solution of picric acid. A yellow precipitate will indicate gelatin in any considerable amount; smaller amounts are shown by a cloudiness. In the absence of gelatin the filtrate obtained will remain quite clear.

**For Fat.**—Make estimation as soon as possible after sample has melted. Weigh 9 grams of the sample in a Babcock cream bottle. Add 30 cc. of a mixture of equal parts by volume of concentrated HCl and 80 per cent.  $\text{CH}_3\text{COOH}$ . Heat on a water bath until well darkened, but *short of charring*. Whirl in a Babcock centrifuge and read the percentage of fat directly. If the cream is charred, add ether after the whirling, draw off the layer containing the fat into another Babcock bottle, evaporate the ether, fill the bottle with water, and again read percentage of fat after whirling.

**Character of Fatty Matter.**—For observing the character of the fat, 30-40 cc. of the cream layer are placed in a Babcock cream bottle, 1 cc. of strong mercuric nitrate solution and 20 cc. of petroleum ether are added, and after whirling, the ethereal layer is separated, washed with water, and the ether evaporated.

### CHEESE.

A product prepared from the caseinogen of milk with or without the fat. The milk is clotted with rennet, sepa-

<sup>1</sup> *Jour. Amer. Chem. Soc.*, 1907.

rated from the whey, ground, salted, pressed into shape and cured. The curing operation consists in subjecting the cheese mass to the action of certain bacteria and moulds, which form acids, hydrolyze the proteins and develop flavor and odor.

Cottage cheese is merely finely divided caseinogen precipitated by the lactic acid of the souring process aided by the heating and undergoes no further change.

Cheeses are usually made from cow's milk but may be produced from goat's or ewe's milk or mixtures of all of them.\*

#### EXPERIMENTS ON CHEESE.

Take a sample of well-cured cheese, grind some of it in warm 5 per cent. NaCl solution, filter and reserve the residue.

Divide the filtrate into four parts and test as follows:

1. For acidity or alkalinity with litmus paper and N/10 acid or alkali.
2. For state of protein matter, by biuret test.
3. For soluble mineral matter, *i. e.*, sulphates, etc.
4. For ammonia and sulphides.

Extract the residue several times with the same portion of hot neutral alcohol, cool, and test the extract with litmus paper for fatty acids. When cold, observe the cloudy precipitate of esters. Separate by filtration and test for free fatty acid and fats.

Divide the extracted residue into two parts and test as follows:

1. For insoluble protein.
2. Burn to white ash and test for insoluble mineral matter—phosphates, lime, etc.

During the incineration, hold pieces of moistened red litmus and lead acetate papers in the fumes and record the results.

\* For further information, see Vulté and Vanderbilt, *Food Industries*, and Wing, *Milk and Milk Products*.

Cheeses are frequently preserved in wrappings saturated with borax or boracic acid solution. To determine this, steep some of the paper wrapping in warm water, filter if necessary, acidify with HCl and dip pieces of turmeric paper in the liquid. Dry these at  $212^{\circ}$  F.; a pink color indicates borates.

## CHAPTER XI.

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### **BAKING POWDERS.**

It is frequently necessary to develop carbon dioxide for leavening purposes more rapidly than by the agency of yeast. For this purpose the purely chemical method by the acid decomposition of carbonates or bicarbonates is most available.

Undoubtedly the time-honored custom of using saleratus (bicarbonate of potash) and sour milk (lactic acid) furnished the original idea on which the modern mixtures were built up. This original idea still survives to some extent in modern practice, but is open to at least two strong objections. First, bicarbonate of potash is no longer a commercial article but is replaced by the cheaper and stronger bicarbonate of soda; still no change is made in the proportions used. Second, it is very difficult to estimate the amount of lactic acid in sour milk by simple means with any accuracy. In fact the quantity is usually largely over-estimated. When milk shows decided indications of the sour stage only  $\frac{4}{10}$  of one per cent. of lactic acid are usually found. It must be remembered that any excess of the bicarbonate used is changed into alkaline normal carbonate by the heat of baking.

For the above stated reasons it can easily be seen that accurately compounded mixtures (leaving neither alkaline nor acid residues), retaining their qualities for some time in the dry state, but ready to develop gas on addition of water, have a decided advantage. In order to preserve these mixtures in a dry state, it has been found

advisable to add to them such agents as raw starch and pulverized lactose, which are perfectly harmless. Such additions should not in any case exceed 25 per cent. of the whole mass. When used for this purpose the compounds are known as "fillers."

Modern baking powders may be classed as tartrate, phosphate, and alum phosphate. All contain bicarbonate of soda, while the acting acid ingredient varies, as follows:

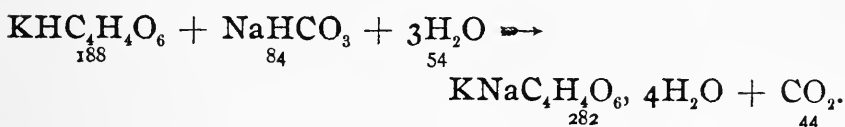
Tartrate—Cream of tartar,  $\text{KHC}_4\text{H}_4\text{O}_6$ , and sometimes a small amount of free tartaric acid,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .

Phosphate—Soluble phosphate of lime,  $\text{CaH}_4(\text{PO}_4)_2$ .

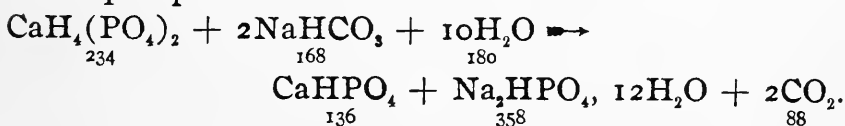
Alum phosphate, same as above with addition of dry alum,  $\text{K}_2$ ,  $\text{Na}_2$ , or  $(\text{NH}_4)_2$ ,  $\text{Al}_2(\text{SO}_4)_4$ .

The following reactions clearly show the changes taking place in using these mixtures:

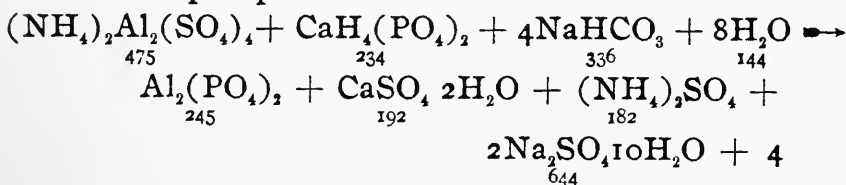
For tartrates:



For phosphates:



For alum phosphates:



It is significant that the tartrate powders leave no insoluble residue except starch, while the others leave nearly one-third of their weight in insoluble mineral matter besides the starch. The phosphates yield the acid soluble phosphate of lime, of doubtful utility, and the alum powders, alumina phosphate and calcium sulphate.

The table of comparison on p. 173 is taken from Vulté and Vanderbilt's *Food Industries*.

An efficient baking powder can be made at home at a low cost by combining the following ingredients:

½ pound cream of tartar.

¼ pound baking soda.

¼ pound cornstarch.

For maximum efficiency these suggestions should be observed: Dry the cornstarch before combining; mix and sift the ingredients thoroughly; either make up small quantities or pack in small tightly closed receptacles.

Ammonium carbonate is sometimes used as a baking powder, since it yields carbon dioxide when heated:



It will be seen that all the products are volatile, no residue being left unless an excess of the powder is used. In that case an unpleasant taste is noticed in the product. The amount of powder required is only about one-tenth as much as of other powders.

#### EXPERIMENTS.

**Tartrates.**—Mixtures of cream of tartar and bicarbonate of soda with starch or lactose filler. Treat a small portion of the powder with water and after the effervescence has ceased test a portion of the liquid for starch with iodine solution and for



	Weight of 1 l. of powder (grams)	Weight of 1 l. of powder less the filler (grams)	Weight of CO <sub>2</sub> (gram)	Volume of CO <sub>2</sub> at 0° C. (cc.)	Volume of CO <sub>2</sub> at the oven tempera- ture (cc.)	Weight of the residue (grams)	Remarks
Tartrate . . . . .	3.0	2.4	0.4	200	273	2.5 (All soluble in water)	Residue con- tains water of crystalli- zation.
Phosphate . . . . .	4.4	3.3	0.72	355	485	4.05 (27.5 per cent. insoluble in water)	Residue con- tains water of crystalli- zation.
Alum phosphate	2.85	1.9	0.32	160	218	2.17 (36.6 per cent. insoluble in water)	Residue con- tains water of crystalli- zation.

lactose with Fehling's solution, boil the remainder of the liquid, cool, filter through fluted paper, and test with litmus paper.

1. Place a few drops of the clear liquid on a slide and allow it to evaporate spontaneously. Examine the cleft rectangular crystals of Rochelle salt.

2. *Fenton's Test.*—Test another portion of the solution by adding 1 drop of fresh cold dilute solution of ferrous sulphate, 1 or 2 drops of peroxide of hydrogen and immediately a large excess of 38° Baumé caustic soda—a violet color appears, due to tartrates. Evaporate the balance of the solution in a porcelain dish, char and gently ignite the residue. Note the odor while carbonizing; what does it suggest? Cool, add water and test with litmus paper; why is it alkaline?

Neutral tartrates will respond to the silver mirror test.

Tartrate powders may contain a small amount of bicarbonate of ammonia. To test for this, heat a portion of the powder in a test tube with caustic soda solution; observe the odor; or hold a strip of moistened red litmus paper over the mouth of the tube.

**Phosphate Powders.**—Calcium hydrogen phosphate, bicarbonate of soda and starch filler. Make a water solution and test for filler as in the case of tartrates. Divide the remainder of the solution into three parts.

1. Add a few drops of the liquid to an excess of ammonium molybdate. Heat gently; a yellow precipitate indicates phosphates.

2. Add ammonium oxalate, and ammonium hydroxide until alkaline and boil—white precipitate indicates calcium. This should give a yellowish red flame on platinum wire.

3. As these powders frequently contain alum it is necessary to make a test. Probably the best method for the determination of alum is to add a portion of the solution to tincture of logwood diluted with 2 or 3 volumes of water, finally adding an equal volume of ammonium carbonate. In the presence of alum the liquid is colored lavender or dark blue.

**Carbon Dioxide Determination by the Scheibler Apparatus.—**

Weigh out 500 milligrams of the baking powder, place in the glass-stoppered bottle belonging to the apparatus. Put a small quantity of water in the gutta percha tube (two-thirds full). The columns of water in the apparatus will be at the same level when the pressure inside of the apparatus is the same as the atmospheric pressure, and this should be the condition when the experiment is started. The gutta percha tube is placed inside the bottle containing the 500 milligrams of baking powder and the apparatus is then connected up. Be sure the relief valve is open when the apparatus is put together and closed immediately afterwards. Incline the generating bottle to allow the water to come in contact with the powder. Observe the evolution of gas. Note the height of the water column. Grasp the generating bottle by the neck and shake vigorously until no more gas is evolved. Immediately afterwards balance the water columns by allowing some water to escape into the overflow flask. Read the figure nearest the level of the water. This reading indicates the per cent. of gas liberated by the addition of water to the baking powder, or in other words, the leavening power of the baking powder. This reading should be in the neighborhood of 10, indicating 100 per cent. efficiency, in a fresh tartrate powder.

## CHAPTER XII.

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### TEA, COFFEE, CHOCOLATE AND COCOA.

Tea consists of the cured, dried and rolled leaves of a variety of plants known as the *Thea*. According to the age of the leaf gathered, there are four well known grades, Pekoe the youngest, Souchong next, Congou next and Bohea the oldest. All these are found in the grades of green or black as the method of curing varies. Green teas are not fermented, black teas are fermented, and since fermentation tends to reduce the amount of tannin, the latter are very generally preferred.

The principal constituents of tea are the alkaloid caffein, tannin, ash, and essential oil. As a rule more caffein is found in black teas than in green, and more tannin and essential oil in the latter.

A proper infusion of tea is made by steeping the leaves in freshly boiled water (preferably slightly hard) just below boiling. Five minutes is sufficient to make the extract, when it will contain the maximum of oil, extract and caffein and the minimum of tannin. It should now be poured off the leaves and used. Boiling or long standing increases the amount of tannin in the infusion, while it does not materially affect the caffein or extract.

### EXPERIMENTS ON TEA.

Make an infusion according to rule given in the text, pour off the clear liquid, filtering if necessary, and examine the leaves with a magnifier. Add a few drops of the clear filtrate to a weak starch solution faintly colored with iodine; if tannin is present the color will fade. Determine caffein in the balance of the extract as follows: Add basic acetate of lead as long as a

precipitate appears, filter, wash slightly, reject the residue, add  $\text{Na}_2\text{HPO}_4$  solution to the clear filtrate to precipitate excess of lead as phosphate, and wash. Concentrate the filtrate to small bulk (25 cc.), cool, transfer to a separatory funnel and add 5-10 cc. of chloroform. Mix well, and after settling draw off the chloroform layer into a weighed porcelain dish and drive off the solvent over hot water. Cool and weigh. Caffein crystallizes in minute colorless needles, possessing a bitter taste.

After removing the chloroform, evaporate some of the tea extract in a clean porcelain dish over hot water and note the large amount of residue, also its color and gummy nature.

**Coffee** consists of the dried, fermented and roasted beans of the *Coffea arabica*—an evergreen shrub. In the roasting process flavor is increased owing to the conversion of a carbohydrate constituent to caramel, and the development of caffeol, an oil to which much of the aroma of coffee is due.

Coffee and tea contain about the same amount of caffein. In addition the chief ingredients of the former are caffetannic acid, cellulose, fat, gum, protein, and a sugar.

French coffee usually contains chicory, the kiln dried root of the wild endive; the drying operation produces caramel at the expense of sugar and hence the water extract is dark in color.

Coffee substitutes are composed of roasted cereals or breads with or without the addition of ground roasted coffee. Their extracts may not be entirely free from caffein and tannin, but in any case will contain less than genuine coffee. The bitter taste and dark color are due to caramel.

**EXPERIMENTS ON COFFEE.**

Grind the roasted beans to a fine powder, throw half a teaspoonful of the powder into a vessel holding cool water, stir well, and note whether any color is imparted to the liquid (chicory).

Moisten 1 tablespoonful of the powder with cold water, add 1 cup of warm water, bring to the boiling-point and boil 2 minutes. Filter through paper or cotton and reserve the clear filtrate for test as follows:

Decolorize a small portion with bone-black and when cold test for starch with iodine. It should be absent; if present the sample contains cereal or bread.

Test another portion for tannin (see tea). Determine presence of caffeine (as under tea), using finely ground, well roasted material, and taking about double the amount used in the case of tea. Chill some of the clear filtrate; should it turn cloudy, make further test for dextrin with alcohol.

Make warm infusions (not boiled) of coffee, chicory, and a blend of the two. Add a small quantity of a saturated solution of cupric acetate to each and filter. Greenish yellow color indicates pure coffee; red brown indicates chicory; yellow brown shows a blend of the two.

Examine thoroughly extracted coffee grounds under the microscope.

Determine quality of ash.

**Notes on Coffee Making.\***—Experiments made to compare the quality and composition of coffee extract prepared from different grades of granulation and by different methods lead to the following conclusions:

1. The finer the granulation the stronger the extract. The structure of the coffee granule appears to be such that fine grinding breaks down minute compartments,

\* Taken from the *Tea and Coffee Trade Journal*, Dec. 1913.

which yield increased flavor and color to the infusion. For example:

Coffee of medium granulation, sifted through a No. 6 sieve, gave 25 per cent. efficiency.

The same coffee, not sifted, 50 per cent. efficiency.

Pulverized coffee, 100 per cent. efficiency.

Therefore, one part of the last will be equal to four parts of the first or two of the second.

2. Fresh granulation is essential. Coffee rapidly depreciates in flavor.

3. Boiling water is twice as efficient in making the extract as water under boiling, *e. g.*, at about 150° F.

4. The principal extraction of value takes place the instant the water boils. If boiling is continued the coffee changes color and becomes muddy, because the coarse fibrous shell is broken down and yields undesirable elements to the infusion. Medium granulation is necessary in making a clear boiled coffee.

5. The use of egg in clarifying is not recommended, as it does not improve the flavor. It is better to strain off the liquor.

The methods of making introduced in the tests were:

*Boiling.*—Boiling water poured on coffee and the infusion allowed to boil for a few minutes.

*Steeping.*—Coffee placed in cold water, brought to a boil, and immediately strained off.

*Percolating.*—In a coffee percolator.

*Filtration.*—Boiling water was made to drip slowly and steadily through pulverized coffee in a muslin bag.

*Scalding.*—Coffee was added to actively boiling water, vigorously stirred for 30 seconds and the infusion filtered immediately.

The composition of the infusions was found to be as follows:

	Per cent. extract	Caffein Grains per cup	Caffetannic acid Grains per cup
1. Boiling (Med. Gran.) ..	2.63	2.58	2.35
2. Boiling (Pulv.).....	2.76	3.72	2.41
3. Steeping (Med.).....	2.42	0.58	2.31
4. Steeping (Pulv.).....	2.58	1.75	2.35
5. Percolating (3 min.)...	1.85	2.86	2.21
6. Percolating (5 min.)...	1.86	2.91	2.90
7. Filtration (Pulv.).....	1.51	2.22	0.29
8. Scalding (Med.).....	1.99	2.35	1.81
9. Scalding (Pulv.).....	2.50	2.92	2.31

From the above, it will be seen that:

1. Boiling yields the greatest amount of extract, and a relatively high amount of caffein and caffetannic acid.

2. Steeping yields a lower amount of caffein than (1), but about as much caffetannic acid. With medium granulation, the least amount of caffein is given.

3. Filtration gives less extract and less acid.

4. Scalding is intermediate between filtration and boiling.

5. Percolating gives a low extract but high acid and high caffein. The reason is that the water in a percolator does not boil over the coffee, but passes over by force of condensation, at a temperature seldom above 150° F. Hence its power of extraction is low, but its



acid and caffein content will be relatively high, as these bodies are soluble in cold water. Caffetannic acid is a hindrance to digestion.

A second series of tests showed the following:

	Extract	Caffein Grains per cup	Caffetannic acid Grains per cup
Boiled (Med.).....	2.60	2.47	2.44
Steeped (Med.) .....	2.30	0.80	2.40
Percolated (Fine) (3 min.)	1.85	2.86	2.21
Percolated (Fine) (5 min.)	1.86	2.91	2.90
Filtered (Pulv.) (½ Quan.)	1.03	1.47	0.19

The conclusion reached in the article quoted is that on the whole the filtration method is the best to employ, since it uses the coffee in the most efficient form and water at its most efficient temperature; the flavor of the infusion is superior; it is almost tannin free, and contains on an average about 1½ grains of caffein per cup.

**Chocolate and Cocoa.**—These products are made from the fermented and dried seeds of the fruit of the *Theobroma cacao*, which resembles the cucumber. After drying and husking, the seeds yield two halves called “nibs.”

The nibs are ground to a fine powder under hot rolls, which melts the large quantity of fat (cocoa butter) present and produces a liquid mass. If this is allowed to run into shallow molds and cooled the product is called chocolate or bitter chocolate. Sugar and vanilla extract are often added to the liquid before cooling, producing sweet or edible chocolate.

If the fluid mass of ground nibs is pressed to remove fat and the remainder is cast in molds and afterward ground, the product is called soluble cocoa. Alkali in small amount is frequently used in the effort to make the cocoa more soluble, but this is a fallacy.

The principal alkaloid in the cocoa bean is theobromine. Caffein is present in small amount.

Cheap grades of cocoa contain considerable quantities of starch and ground cocoa shells.

#### EXPERIMENTS ON CHOCOLATE AND COCOA.

Boil some of the finely ground mass with water, filter while hot and reserve both filtrate and residue for test.

*Tests on Filtrate.*—For starch, dextrin, sugar, protein matter and soaps.

*Tests on Residue.*—Dry and extract fatty matter with gasoline. Examine extracted residue under the microscope for fiber. Determine quality and amount of ash.

## CHAPTER XIII.

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### FERMENTS AND PRESERVATIVES.

The organisms which cause the most common changes in our food materials are generally known as yeasts, lactic acid and vinegar ferments. Their spores are present in all house dust. These organisms are distinguished by the fact that they operate in presence of air, under widely varying temperature conditions, and give off no disagreeable odors while their products are non-poisonous. It is true that putrefactive bacteria play some part in the preparation of our food, notably in meats and cheeses, but great care must be observed that the process is kept under strict control and allowed to proceed only to a limited extent. The activities of these various organisms are due to enzymes secreted by their cells.

**Yeast Fermentation.**—This type of fermentation is typically alcoholic. The food chosen for the growth of the yeast organisms is mostly carbohydrate material, which is decomposed by enzyme action to alcohol and carbon dioxide as the principal products. The by-products are extremely numerous, and include succinic acid, glycerol, and traces of esters, aldehydes and complex alcohols. The expression  $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$  is therefore merely general for yeast action.

In ordinary yeast the enzymes acting on carbohydrate material are maltase, invertase, and zymase. There is evidence that phosphates, such as are present in yeast

cells, are necessary to fermentative changes, as added phosphates greatly stimulate fermentation and enter into combination with monosaccharid material as a hexose-phosphate.

Due to the specific action of the enzymes present, starch and lactose are not acted upon directly by ordinary yeast; maltose is changed by maltase to glucose; cane sugar is hydrolyzed by invertase, and zymase completes the alcoholic fermentation of the monosaccharid products. Different yeasts have different fermenting action, *e. g.*, *S. fragilis*, found in kefir, has a lactose enzyme.

Yeasts in general have their optimum activity between 68° and 90° F.; the maximum growth temperature for many varieties is about 105° F. In the moist condition coagulation takes place at lower temperatures than in the dry. Yeasts are killed more or less quickly from 111° to 140° F., with moist heat. Sterilization with dry heat necessitates long continued high temperatures, or intermittent sterilization. For pasteurization, it is well to maintain for some time the lower temperature employed, to insure uniform heating of the mass. Yeasts are not easily destroyed by cold unless exposed to very low temperature for long periods.

The rate of fermentation increases with concentration of the sugar up to a certain limit, then decreases with further concentration. When 15 per cent of alcohol has been formed the action ceases, even though the mass contains unchanged carbohydrate.

**Lactic Acid Fermentation.**—The organisms capable of

producing this form of fermentation are numerous, and operate on various forms of carbohydrate material. They have been found in milk, beer, distiller's mash, sauerkraut, and other substances. The forms most commonly occurring in milk are the *Streptococcus lacticus*, and a similar organism, *Bacterium lactis acidii*, which hydrolyze lactose, and convert the resulting glucose almost entirely into lactic acid:  $C_6H_{12}O_6 \rightarrow 2C_3H_6O_3$ , with no gas formation. Another organism well known for its value in preparing sour milk is *B. bulgaricum*. It hydrolyzes lactose and ferments about 92 per cent. of both products—galactose and glucose—to lactic acid so that the total amount formed is much greater than with the organisms described above. These ferments are not easily destroyed by cold but do not act below 50° F. and continue their work up to 130° F., being most active at 110° F. Conditions for sterilization and pasteurization are similar to yeasts.

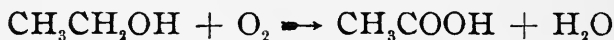
These organisms represent the true lactic fermentation, in which the by-products are almost negligible. A modified lactic fermentation is produced by groups of intestinal origin. The products of these are lactic and other acids, alcohol and gases—lactic acid forming less than one half of the total.

Salt-rising bread\* and sour dough bread are prepared by a method of spontaneous fermentation. The organisms producing fermentation probably vary, but in some instances are those which develop lactic acid and gas

\* See Buchanan; *Household Bacteriology*, and *The Baker's Review*, August, 1911, to March, 1912.

from sugar. When corn meal has been used in the fermenting batter, it is probable that gas is produced by the *Bacillus coli*.

**Acetic Acid Fermentation.**—The production of acetic acid from alcohol is a type of bacterial action well known in everyday experience. The souring of wines and the production of vinegar are illustrations of the activities of this organism. The ferment, commonly known as “mother of vinegar,” carries oxygen from the air to the alcohol, the oxidation resulting in acetic acid:



It acts on all weak alcoholic liquids of 10 per cent. and under. The temperature conditions are much the same as for lactic acid (50°-110° F.). Fermentation ceases when 5 per cent. of acid has been produced. Conditions for sterilization and pasteurization are similar to yeasts.

**Butyric Acid Fermentation.**—Important fermentative changes producing butyric acid are brought about by the action of many bacteria. Two types of these organisms are recognized:

(1) The non-motile butyric acid bacillus, found in milk and in the soil. It is an anaërobic form which ferments sugars, starch, and under some conditions lactic acid, the products being butyric acid, lactic acid, hydrogen, and carbon dioxide. It liquefies gelatin.

(2) The motile butyric acid bacillus, found in soil, water, and cheese. It is anaërobic, does not liquefy gelatin, and has a chemical action on carbohydrates similar to the non-motile form.

Other forms are known, of a pathogenic order, which act upon both carbohydrates and proteins.

### EXPERIMENTS.

**1. Fermentation of Carbohydrate by Yeast.**—Dissolve a considerable quantity—about 150 grams—of commercial glucose or of molasses in 1 or 2 liters of water in a good sized distilling flask. Dissolve one-fourth of a yeast cake, add to the solution, warm to 25° and keep in a warm place until fermentation ceases. Distil over a water-bath, noting the temperature at which the distillate passes over, and test the latter for alcohol by burning a portion and by the iodoform reaction.

**Yeast—Temperature Experiments.**—Prepare four 6-inch test tubes with perforated corks, bearing tubes bent in the form of an inverted letter J. Fill three of the tubes with a mixture, prepared from one-half a yeast cake, one-half tablespoonful of molasses and a cup of water. Fill the fourth with the same preparation filtered through absorbent cotton. Allow tubes Nos. 1 and 4 to stand, while No. 2 is subjected to a temperature of 32° F. (produced by a mixture of pulverized ice and salt) for 15 minutes. No. 3 is boiled for 2 or 3 minutes. Now place the four pieces of apparatus so that the delivery tube of each reaches to the bottom of a test tube containing about 2 inches of clear limewater, and allow them to stand for at least 12 hours in a warm place (90° F.). At the end of this time examine each tube of limewater, first for a precipitate, and second with litmus paper. Finally examine the liquid in the fermentation tubes, noting its odor and general properties.

For the action of yeast on different carbohydrates, see p. 98.

**Lactic Acid.**—To about 6 ounces of pasteurized milk contained in a small flask, add 1 tablespoonful of the liquid obtained by dissolving one lactobacilline (Metchnikoff) tablet in half a cup of tepid water. Mix well and keep at 100° F. for 36 hours. Carefully observe all changes taking place and compare with the well known buttermilk.

**Acetous Fermentation.**—Make a weak solution of alcohol in water (5 parts of alcohol to 20 parts of water) and test with litmus paper; if acid, neutralize with a weak solution of sodium carbonate and test a small portion with potassium iodide and potassium hydroxide, heat—the odor of iodoform shows the presence of alcohol.

Divide the balance of the solution into two equal parts, pour one into a shallow dish and place the other in a well-corked bottle. After the solutions have stood for a week, test with litmus paper, and also by adding alcohol and warming gently. Note the peculiar odor of ethyl acetate—odor of hard cider—in the first case but not in the latter. Explain.

Expose a small quantity of beer to the atmosphere for several days; subsequently examine for acidity with test paper and for acetic acid with alcohol. From the results of these experiments explain why bottled weak alcoholic beverages keep sweet.

**Butyric Fermentation.**—Neutralize some sour milk with chalk, add a little decaying cheese, and allow to stand for some hours. The butyric ferment in the cheese acts on the lactic acid in a neutral medium, as follows:



Note the growing acidity and odor of the milk.

All foods are subject to the attack of bacteria and in consequence their value is very generally seriously impaired. Methods for prevention of these changes have been used from the earliest times and are known as preservation.

At least two general types of process are in common use, *viz.*, physical and chemical. To the first class belong such methods as drying, cooling, and canning. These processes are applicable to all kinds of foods, possess high efficiency and make very slight changes in flavor, appearance and composition. Unfortunately, food ma-



terials preserved in any of these ways will change very rapidly with a slight variation of physical conditions, hence the effects are not permanent. The second class involves such change of chemical conditions that no matter what physical changes may occur, decomposition cannot take place. The results are permanent but are accomplished at the expense of flavor, appearance, etc.

So general has the use of chemical preservatives become that a brief discussion of the subject seems necessary. The best known and, as generally conceded, harmless are: alcohol, vinegar, sugar, and salt ( $\text{NaCl}$ ). With the exception of vinegar (acids generally being inimical to bacteria) the action seems to depend on making the protein matter present insoluble; hence we find the quantity of the preservatives important. Well known operations are as follows:

Alcohol—50 per cent. "Brandyng."

Salt—dry or supersaturated solution "Pickle."

Sugar—syrup—solutions of 25 per cent. or more.

Less well known methods accomplish similar results by using very small, in some cases minute proportions, of other chemical agents; but the actual chemical operation can only be surmised in most cases. Included in this list are: borates, fluorides, sulphites, peroxides, formaldehyde, benzoates, salicylates and creosote. It may be as well to observe that the use of spices, for instance in mince meat, is certainly parallel with benzoates and salicylates.

Boric acid, borax and borates are efficient in small

quantities—as low as 1 per cent. Their use in preserving meats is not permitted at present in the United States.

Sulphites can not now be used for giving cut meat a red appearance.

It has not been proved that sodium benzoate is dangerous in the amounts used for food preservation, and it is allowed under the Food and Drugs Act, provided the label states the fact. Salicylic acid is not allowed.

Wood tar creosote is very efficient as a non-poisonous preserver of meat.

### EXPERIMENTS.

Alcohol and vinegar are first separated by distillation and then identified by well known methods. Sugar and salt may also be determined by diluting, filtering and testing the clear filtrate.

*Borates.*—Ash some of the substance, cool, make strong water extract, filter if necessary and neutralize with dilute HCl. Dip a strip of turmeric paper in this liquid, remove and dry by steam heat. (This may be accomplished by wrapping the moist paper around the upper part of a test tube partly filled with water and boiling gently.) The paper turns pink on the edges.

Or moisten the ash in the dish with alcohol, add 8 to 10 drops of glycerine, mix well with a glass rod and ignite the mass with a match or Bunsen burner. Note the yellow flame with a green edge, characteristic of borates.

*Fluorides.*—Mix the liquid or solid mass with an excess of limewater, evaporate to dryness, ignite, cool and make the etching test.

*Sulphites.*—If present in quantity, they are distinguished by their odor and taste, "sulphur match," especially on warming.

For small amounts of sulphites, mix with bromine water, boil off excess and test for sulphates. Sulphates may be present in the original liquid, in which case precipitate by  $\text{BaCl}_2$  and HCl, filter and use the clear filtrate as above.

*Formaldehyde.*—See page 199.

*Benzoates.*—Carefully mix liquid substance with one-tenth of its volume of chloroform and a few drops of oil of vitriol. Avoid violent shaking (mix with a rotary motion). Allow the mixture to remain quiet until chloroform layer separates. Remove some of this layer with a pipette and evaporate it in a clean porcelain dish over hot  $H_2O$ . Note the flat crystalline plates of benzoic acid, which give off a pungent odor on heating. Examine the original mixture in the flask, note any violet color between layers of acid liquid and chloroform. This indicates salicylic acid.

Both benzoic and salicylic acids are not present in the same liquid.

### TESTS FOR PURITY OF CERTAIN FOODS.

**Sanitary Condition of Milk.**—The presence of a large number of bacteria in milk indicates staleness or an insanitary condition. The following test will give some indication of its purity: First sterilize all utensils used by keeping in boiling water  $\frac{1}{2}$  hour. Warm 1 pint of milk to body temperature and add one junket tablet which has been dissolved in 1 tablespoon of cooled boiled water. Stir until thoroughly mixed and allow to stand quietly until the milk has clotted. Cut the curd in cross-sections with a knife and carefully pour off the whey. From time to time, draw off the whey as it accumulates. When the curd is compact, cut it with a knife and observe its condition. If it is firm and smooth with but few holes, the milk does not contain an abnormal number of bacteria. If the curd has a spongy appearance, bacteria are present which have produced gas. Place a tablespoon of the curd in water; if it sinks, the milk is comparatively clean; if it floats, the milk is stale or in an insanitary condition.

**Formalin in Milk.**—See page 166.

**Genuine Butter.**—See page 140.

**Coal Tar Coloring in Butter, etc.**—1. The custom of coloring butter is very largely practiced in the United States. Vegetable dyes, such as annatto, have been employed in the past, but coal

tar products (anilin dyes) are now quite frequently used. Coal tar yellow may be detected by the following experiment: Into a weak solution of alcohol, put 1 teaspoon of butter, a small amount of cream of tartar, and bits of white silk or wool. Boil the mixture. If coal tar coloring is present, the samples will be dyed.

2. Melt a teaspoonful of butter in a test tube at low heat. Add an equal volume of Low's reagent (mix 4 parts  $\text{CH}_3\text{COOH}$ , 1 part  $\text{H}_2\text{SO}_4$ ); shake well, heat nearly to boiling, and set aside to separate into layers. The acid layer will be colored red if azo dyes have been used. Pure butter gives a faint blue tinge.

**Annatto.**—Place about 100 cc. of milk in a cylinder, make alkaline with sodium carbonate solution, insert a long strip of heavy white filter paper and allow to stand in a dark place for about 12 hours. Withdraw the paper, wash gently in running water and observe against a fresh piece of the same kind of paper. If annatto is present, the paper will have taken up some of the color. Prove by dipping the strip into a solution of stannous chloride. It becomes pink.

**Alum in Food Products.**—Make water solution and follow method under Baking Powders, page 174.

**Copper Compounds in Canned Goods.**—As a rule, coloring matter is not added to domestic goods. Imported varieties, as green peas, having an intense color, usually have copper added in small amounts. It may be detected by adding a few drops of hydrochloric acid to a portion of the material and dropping in a bright steel nail or the blade of a knife. If copper salts are present, a reddish color will appear on the steel.

**Purity of Olive Oil.**—See Halphen's Test, page 139.

**Purity of Extracts.**—*Vanilla.*—(a) Vanilla extract shows a nearly colorless foam on shaking; in case vanillin has been used the foam will be colored due to the addition of caramel for the purpose of imitating the vanilla color.

(b) *Leach's Test.*—To 40 cc. of the sample add an equal volume of normal lead acetate (dissolve 189.5 grams of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  in water and make up to 1 liter). If a

precipitate settles out the vanilla is pure; vanillin gives no precipitate.

**Lemon Extract.**—Test by adding a few drops of the extract to water. The true lemon oil is insoluble in water, and a milky appearance results. Artificial lemon extract gives a clear water solution.

**Saccharin.**—This substance may be added to canned products in place of sugar. It is a coal tar product having several hundred times the sweetening power of cane sugar. To determine its presence shake 15 or 20 cc. of the suspected liquid in a flask with an equal volume of chloroform. Saccharin is soluble in chloroform; while sugar is insoluble. With a medicine dropper remove some of the chloroform which has settled to the bottom. By gently heating in a porcelain dish, evaporate the chloroform. Taste the residue; if sweet, saccharin is present.

**Freshness of Eggs.**—Candling is one of the methods most frequently used. In a darkened room hold an egg between the eye and an artificial light. A fresh egg should appear unclouded, homogeneous, and almost translucent. If dark spots are found, it is stale. A rotten egg appears dark colored.

Against the larger end of a fresh egg between the shell and the lining membrane, a small air cell should be distinctly visible. In an egg which is not perfectly fresh, this space is filled with the egg substance, unless the egg has been stored with the large end up.

**Salt solution test:** As the density of an egg decreases by the evaporation of moisture, its freshness may be approximately estimated by placing it in brine. Prepare the salt solution by dissolving 2 ounces of salt to 1 pint of water. Immerse the egg in the solution. A perfectly fresh egg will sink; if several days old, it will swim just immersed in the liquid; if stale, it will float on the surface.

Shake an egg, holding it near the ear. The contents of a fresh egg should not move. If a slight movement can be detected, it is somewhat stale; if it rattles, the egg is spoiled.

Open the egg and observe the odor and taste. If there is a tendency for the white and yolk to run together, the egg is not fresh, or the hen has been improperly fed.

**Coffee.**—See Experiments, page 178.

**Gelatin in Ice Cream.**—Page 167.

Vinegar has been very largely subject to substitution and imitation. The best varieties on our market are cider, wine, and malt vinegar. Substitution may be detected by slowly evaporating almost to dryness  $\frac{1}{2}$  cup of vinegar in a small evaporating dish and examining the warm residue. If there is a distinct odor of baked apples, it is cider vinegar; of grapes, it is wine; and of malt, the product is malt vinegar. Distilled vinegar gives a burnt sugar odor; no residue indicates synthetic vinegar.

## CHAPTER XIV.

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### DISINFECTANTS AND DISINFECTION.

These terms apply to the destruction of bacterial organisms and their spores. Some confusion of ideas exists with regard to the respective action of disinfectants and antiseptics. A disinfectant is a germicide; an antiseptic retards or prevents bacterial activity. A deodorant simply absorbs or covers up noxious vapors.

**Physical Methods of Disinfection or Antisepsis.**—*Sunlight.*—The direct rays of the sun are powerful enemies of bacteria, the bacillus of tuberculosis, for example, being killed by sunlight.

*Dry Air.*—Dry air arrests the activities of bacteria by removing conditions of moisture favorable for their growth, and oxidizes the products of their action through the work of aërobic organisms in the air.

*Cold Storage.*—This is an efficient temporary method of inhibiting bacterial activity. It should be understood that freezing and cold storage are not the same. In freezing, the expansion of the ice crystals disrupts the structure of food and leaves it open to attack. Food that has been frozen should therefore be consumed as soon as possible after thawing.

*Pasteurization.*—Bacteria likely to be present in impure milk are killed by a temperature of 60° to 70° maintained for 20 minutes to 1 hour, according to the temperature employed. The organisms which escape are comparatively harmless in effect.

*Boiling.*—Typhoid and tuberculosis bacteria are killed by boiling for 1 minute. Drinking water and milk are likely to be sterilized by this treatment. To destroy the spores of some other forms of pathogenic bacteria, boiling must be repeated on two or three successive days.

**Some Common Antiseptics.**—Salt, sugar, spices, vinegar, and creosote have considerable efficiency as antiseptics. The power of salt, sugar, and vinegar to inhibit the action of bacteria depends upon the strength of their solutions.

**Chemical Means of Disinfection.**—*Mercuric Chloride*, or corrosive sublimate, is one of the most powerful of germicides. Its use is limited, partly because it is a violent poison, partly by its tendency to form a precipitate with many inorganic and organic substances, such as hard water, alkalis, protein bodies, etc. A solution of one part of mercuric chloride in one thousand parts of water is commonly employed.

*Carbolic Acid.*—This is frequently used in very dilute solution as an antiseptic wash, as a powerful antiseptic in a strength of 1 to 400, or as a germicide in stronger solution, such as 5 per cent.

*Formaldehyde.*—Formaldehyde is antiseptic in weak solution, and germicidal in the 40 per cent. solution called formalin. For room disinfection the formaldehyde gas is used, produced by lamps which pass methyl alcohol vapor and air over hot oxidized copper, or by heating paraform. This substance is a solid polymer of formaldehyde, which gives off the gas when heated. Formaldehyde is also produced from formalin heated under



pressure, or treated with dehydrating agents to cause an evolution of the gas.

*Sulphur Dioxide*.—This is a powerful disinfectant, but has the disadvantage of being also a strong bleaching agent, and therefore cannot be used in the presence of colors. The gas is produced by burning sulphur, commonly in the form of a sulphur candle. It is irrespirable, and has produced fatal results when in the proportion of about 5 per cent. in air. To do away with the necessity of using fire to produce sulphur dioxide, its solution in water as sulphurous acid is frequently used. This acid is unstable, and when exposed to the air gives off sulphur dioxide and water.

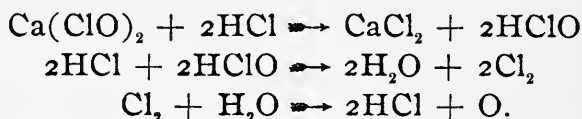
*Copper Sulphate*.—This compound ranks next to mercuric chloride in antiseptic power. It is soluble in four parts of water, and in 1 per cent. solution is disinfectant; in weak solution, *e. g.*, 0.1 per cent., it is antiseptic in most cases.

*Zinc Chloride* is strongly antiseptic and disinfectant, and is useful for drains. A solution of 1 to 5 per cent. is employed for ordinary antiseptic purposes. Zinc oxide is much used in the preparation of cold creams and ointments, and is a mild antiseptic.

*Hydrogen Peroxide* is a powerful oxidizing agent, as it decomposes into water and nascent oxygen. It has a bleaching action on fabrics, but is not as destructive to the material as are Javelle water or bleaching powder. As a disinfectant it is comparatively slow in its action, but the evolution of oxygen is hastened by the addition of a small amount of an alkali, such as borax, to the

solution. In dilute solution hydrogen peroxide is non-poisonous.

*“Chloride of Lime” or Bleaching Powder.*—So-called chloride of lime, used for disinfecting purposes, is calcium hypochlorite,  $\text{Ca}(\text{ClO})_2$ . A similar compound, sodium hypochlorite, is known as Javelle water. The action of both depends upon the available chlorine they contain, which when set free unites with water to form eventually hydrochloric acid and nascent oxygen. The carbon dioxide of the air, or other acid present, is necessary to bring around the reaction. Using acid:



Both hypochlorites are strong bleaching agents and are especially destructive to wool and silk fabrics. Cotton and linen materials are not seriously affected, but should be rinsed free from bleaching powder or Javelle water if these are used for disinfecting clothes. The latter solution is better for this purpose. Bleaching powder is often used for drains in about 10 per cent. solution.

*Washing Soda.*—In the strength used in the laundry, washing soda has little antiseptic effect, but is efficient in about 2 per cent. hot solution as a disinfectant for washing floors and walks, milk cans, etc.

*Soap* has considerable antiseptic power. So-called disinfectant soaps have little advantage over ordinary pure soaps unless the proportion of disinfecting ingredient is high, and it is in readily soluble form.

### Tests for Disinfectants.

On account of the small quantities of material usually employed, many of the ordinary analytical tests fail to give conclusive results. Hence the following methods are suggested, as being more reliable in the majority of cases.

**Mercuric Chloride.** (Found usually in one or two parts, or less, per thousand.)—To 50 cc. of the solution in a large test tube add a few cc. of a mixture of equal parts of weak potassium iodide and ammonium chloride solutions (each 1 per cent.) and immediately 2 or 3 drops of caustic soda. A yellow color or brown precipitate developing after a few minutes' standing indicates mercury. It will be noticed that this test is a reversal of Nessler's test.

**Carbolic Acid.**—To the clear liquid add bromine water in slight excess and immerse in hot water until all odor of bromine is dissipated. A white bulky precipitate of bromphenol indicates carbolic acid.

**Formaldehyde** is best indicated by the violet band appearing as a zone when the liquid containing the aldehyde is carefully poured upon a large volume (10 cc.) of commercial concentrated sulphuric acid (oil of vitriol) held in a test tube. The color is due to ferric salt always present in the crude form of the acid.

**Sulphur Dioxide or Sulphites.**—Indicated by warming the acidified (HCl) solution—an odor of burning sulphur is apparent. Or by adding barium chloride to the acidified solution, boiling, and filtering off the first precipitate (a precaution necessary due to the presence of sulphates), finally adding a few drops of nitric acid to the clear filtrate and boiling again until oxides of nitrogen and chlorine are expelled. A white precipitate of barium sulphate remains, insoluble in hydrochloric acid.

**Copper Sulphate.**—Indicated by a deep blue color on adding ammonium hydroxide in excess, or by a reddish brown precipitate in potassium ferrocyanide solution acidified with acetic acid.

**Ferrous Sulphate.**—Indicated by a deep blue precipitate in contact with dilute potassium ferricyanide solution, which decomposes on addition of sodium hydroxide and leaves a brownish residue.

**Permanganates.** (Alkaline potassium or sodium).—Impart a pinkish color to the liquid even in dilute solution. The color is quickly discharged on adding a mixture of dilute sulphuric and oxalic acids and warming, or by a few drops of fresh ferrous sulphate solution acidified with dilute sulphuric acid.

**Hydrogen Peroxide.**—Indicated by the deep blue shade imparted to ether when in contact with an acidified mixture of potassium dichromate and peroxide.

**Bleaching Powder ("Chloride of Lime").**—Sets free the halogen from potassium or sodium iodides. If chloroform is added the iodine dissolves in it with a violet color. In the presence of starch, the iodide of starch (blue color) is formed.

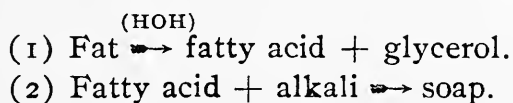
## CHAPTER XV.

### CLEANSING AGENTS.

The number of compounds put on the market for household use in cleansing and allied operations is constantly increasing, and in many cases extravagant claims are made with regard to the efficacy of the preparations. The public is led to believe that each one represents the discovery of a new and powerful detergent. As a matter of fact, analyses of these preparations show that they are merely variations in combination of a few well known cleansing agents. A general classification of cleansers and similar compounds reduces them to a few principal groups:

1. Soaps and soap powders.
2. Scouring powders.
3. Metal polishes.
4. Bleaches and stain removers.
5. Grease solvents.
6. Bluings.

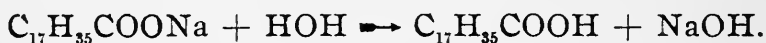
**Soap and Soap Powders.**—As shown in Chapter IX, soaps are a product of the saponification of a fat by an alkali. Sodium or potassium hydroxide is commonly used. The type formation of the soap is as follows:



It will be seen that glycerol is a by-product. It is recovered in the commercial method of soapmaking, a

process which gives the market its chief supply of this commodity.

*The Cleansing Action* of soap is both physical and chemical. Its solution in water acts as an emulsifying agent, loosening and removing dirt particles. Chemically, soaps are salts of a strong base and a weak acid, and as such dissociate in water with some hydrolysis, *e. g.*:



The alkali set free may form additional soaps with free fatty acids present in the greasy impurities of the article to be cleansed.

*Soap powders* contain dry pulverized soap, together with an excess of sodium carbonate in the hydrated form. They may or may not contain insoluble mineral matter—clay, sand, etc.—and trifling amounts of borax.

**Manufacture of Soap.**—Two classes of water-soluble soaps are recognized—hard, or soda, and soft, or potash soaps. In the former the harder fats and non-drying oils are used as a rule; for the latter vegetable drying oils and marine animal oils are utilizable. In the manufacture of hard soaps two methods—the cold process or boiling—may be employed. The *hot process* is the usual commercial method, as the soap produced is more apt to be uniform in appearance and quality, and glycerol can be recovered as a by-product. The *cold process* gives a simple and quick method for household use, and if operated with intelligence gives a good neutral soap, which contains the glycerol.

*Boiled Soap.*—The saponification process is divided into at least four stages, although a number of intermediate stages called “washes” are frequently introduced to remove impurities.

The four changes are known as :

Stock change.

Rosin change—where no rosin is used this change is replaced with a wash.

Strength change.

Finish.

*Stock Change.*—The required amount of mixed tallow and grease or oil are melted together in large iron kettles or tanks by the aid of steam coils, the lye is added and the whole mass boiled until it is saponified; at this stage the mass of boiling soap has a peculiar smooth appearance called “closed.” Pickle is now added, until the contents of the kettle separate into small broken grains; this stage is called “open or grained.” Heat is turned off and the kettle allowed to cool; when cold there will be two layers, the upper one of soap, floating on the salt lye—this latter is called “spent lye” and should be almost neutral. From it glycerine and salt may be extracted. The spent lye is then drawn off from the bottom of the kettle, leaving the soap for the next operation. If no rosin is to be used the “wash change” takes place at this point; this consists in adding water, boiling to a “close” and then salting out and settling as before; the wash lye is worked up for salt and glycerine.

*Rosin Change.*—Soap from previous operation receives

an addition of fresh, strong lye, is heated to boiling and the rosin in lumps thrown into the kettle; only just enough lye to saponify the rosin is used; the amount of rosin varies but usually equals the weight of the tallow and grease. Boiling is continued until rosin is saponified, and then pickle is added to grain; the kettle stands to cool; the rosin fat soap rises as before and the rosin lye is drawn off and worked for salt and traces of glycerine.

*Strength Change.*—The rosin fat soap is now boiled with fresh strong lye until saponification is complete. It is always found that small amounts of fat and rosin escape saponification in the earlier stages unless these are unduly prolonged. Kettle is cooled and the soap which has been grained or open condition throughout this operation (due to strong lye) rises; when cold the strong lye is drawn off and used to start the saponification in the stock change. This lye is often mixed with that coming from the strength change.

*Finish.*—The thoroughly saponified grained soap still contains strong lye and many impurities; and this is removed by melting and adding water carefully until the soap “closes,” or loses its grained structure. The kettle is allowed to cool very slowly, being kept perfectly quiet for at least 48 hours. During this time three layers are formed, the upper consisting of pure soap, the intermediate of impure dark soap called “nigre,” which may be sold as such or bleached in a subsequent operation, and a very small amount of strong alkaline lye called the nigre lye, which is generally thrown away.



The finished soap is either run into iron box moulds, stirred well, and allowed to cool and set thoroughly, and then cut; or is run into a "crutcher" or mixing machine, where various additions, such as sal soda, silicate, saponified rosin, etc., are made. From this machine the mixture is run into frames, cooled and cut.

*Half Boiled Soap.*—Much of the ordinary toilet soap is made by this process, which is as follows:

The requisite quantity of fat, tallow, grease, cotton seed or coconut oil is heated gently in a jacketed steam kettle, enough very strong lye usually mixed; potash or soda is gradually added and stirred vigorously; the operation is complete when the hot soap is clear and will run in long strings from the trowel or stirrer. The mixture is now ladled into frames and allowed to cool and set. When cold it is removed from the frame, cut into strips, dried, chipped, milled between stone rollers. In the milling operation, coloring matter and perfumery are added, although for cheap soaps these additions may be made in the kettle after saponification. After milling the soap goes through the "plotter," which forms it into long bars and cuts these into convenient lengths for pressing. It will be noted that the glycerine remains with the finished soap in this process. The best toilet soap is made by the full-boiled process.

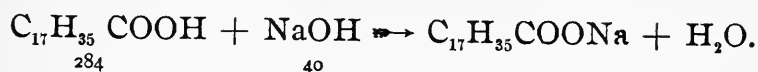
*Average Analyses.*—The average compositions of a white laundry soap of good quality and a yellow soap containing rosin are given below for comparison:

	Rosin soap per cent.	White soap per cent.
Water .....	30.0	15—25
Combined fat as actual soap .....	30.0	85—75
Rosin.....	35.0	
$\text{Na}_2\text{CO}_3$ .....	3.5	
Mineral matter, including NaCl .....	1.0	
Free caustic.....	0.5	
	100.0	100.0

*Use of Rosin.*—Rosin is cheaper than soap grease, and is introduced primarily as a filler. It is properly classed as an adulterant. By its presence more water can be incorporated with the soap, hence rosin soaps soften and waste away rapidly. It is not strictly a detergent, except as it aids in making a suds, and its continued use has a yellowing effect on white fabrics. Based on the amount of actual soap contained in soaps of this class, they cost more per pound than a good grade of white soap.

*Cold Soaps.*—For the production of a neutral soap by this process, the correct combining amounts of fat and alkali must be determined. The mean saponification numbers of the fats and oils commonly used call for a proportion of 1 gram of fat to 0.195 gram of KOH, or 0.139 gram of NaOH, *i. e.*, ratios of 5:1 and 7:1 respectively. Therefore, in practice, 5 units of fat by weight combine with 1 unit of caustic potash, or 7 units with one of caustic soda. This calculation is approxi-

mated by taking the combining weights of the interacting substances:



Here 284 units of weight combine with 40, giving a ratio of 7:1.

In round numbers, for 7 pounds of fat, use 1 pound of caustic soda, dissolved in water to a suitable bulk. Crude caustic soda, costing a few cents per pound, can usually be obtained. The consistency of the fat largely determines the amount of water which may be incorporated; a fat liquid at ordinary temperatures will take up only about enough to dissolve the alkali, more solid fats will hold water in amounts varying from one-half the weight of fat to equal weights of the two.

The process of making cold soap consists in melting the fat, stirring in the dissolved caustic soda until a homogeneous, creamy mass is obtained, and setting the mixture aside in molds to complete the saponification and harden. Twenty-four hours usually suffices. Some household recipes are appended, made on the basis of 1 pound of fat. To obviate weighing  $\frac{1}{7}$  of a pound of the alkali, it is convenient to dissolve a pound in the right amount of water, and measure out the particular quantity required.

*Laundry Soap.*— $\frac{1}{7}$  pound NaOH dissolved in sufficient water to make 14 fluid ounces ( $1\frac{7}{8}$  cups). Strength  $17^\circ$  Baumé.

1 pound solid fat melted.

*Emulsion Soap.*—Add to the above before it hardens, 3 tablespoonfuls each of kerosene and a strong solution of washing soda. Stir about 5 minutes longer. Incorporate 1 pint of water for a soft soap.

*Castile.*— $\frac{1}{7}$  pound NaOH made up to  $\frac{1}{2}$  cup with water. (38° Baumé.)

1 pound olive oil.

*Coconut Oil.*— $\frac{1}{5}$  pound (full weight) NaOH made up to 1 cup.

1 pound coconut oil.

(The exact proportions are  $5\frac{1}{2}$  pounds oil to 1 pound NaOH.)

By stirring in air with an egg beater, the result will be floating soap.

*Palm Oil.*— $\frac{1}{7}$  pound NaOH made up to  $1\frac{1}{4}$  cups.

1 pound palm oil.

*Special Varieties—Scouring Soaps.*—These are made by introducing into the soap while in a creamy condition, a large amount of finely pulverized quartz or other mineral matter.

*Transparent Soaps.*—Such soaps are made by incorporating the amount of alcohol required to hold the soap in a clear solid solution. In some cases the transparency is produced by the use of sugar, which must be considered an adulterant.

Liquid soaps are soap solutions containing an excess of the solvent.

**Soap Analysis.**—For detailed methods, see Chapter XVI. As a simple means of determining whether a soap is superfatted or contains excess alkali, apply the following tests:

### TESTS.

*For Free Fat.*—Shake a few shavings of the soap in a corked test tube with cold gasoline, filter into a convex glass and evaporate the gasoline over warm water. A greasy residue indicates unsaponified fat.

*For Free Alkali.*—Shake a few shavings of the soap in a corked test tube with warm alcohol (95 per cent.), filter and add to the clear liquid a few drops of phenolphthalein; a red color indicates free alkali. Or, drop some of an alcoholic solution of phenolphthalein on the freshly cut surface of the soap.

**Scouring Powders.**—These are improved forms of the old crude mixtures of sand and soap, formerly used extensively for rough cleaning. They now consist of clay, incorporated for absorbent purposes, and pulverized soap, containing abrasive material in a more or less finely divided condition. Borax may be present, and at times clay is partly or entirely replaced by chalk. The common fault with such preparations is that their use is recommended for general cleaning, but they frequently contain sharp abrasive particles which make them injurious to fine metal or porcelain surfaces.

Average analyses of these powders are appended:

	Per cent.
Water .....	1—6
Soap .....	4—14
Sodium carbonate .....	0—24
Abrasive material .....	63—93

**Metal Polishes.**—These polishing agents are on the market in liquid, paste, and powder forms, also as polishing cloths. Their action in removing tarnishes—oxide, sulphide or carbonate coatings—depends upon the abrasive effect of pulverized mineral material, the solvent action of chemicals, or both combined.

*The liquid polishes* are solutions containing as a rule one or more of the following ingredients: oxalic acid, muriatic acid, ammonia, benzine or benzene, and potassium cyanide. These may be combined with pulverized mineral matter.

*Oxalic acid* is very effective in dissolving metallic oxides and carbonates, and is therefore in common use as a cleanser for brass and other metals. The acid potassium oxalates are similarly used. The metal itself is liable to be attacked by oxalic acid, which should not be used in too strong solution for nickel-plated faucets, etc.

The cleansing effect of muriatic acid is similar to that of oxalic, and can be produced in the household by using a mixture of salt and vinegar.

*Ammonia* is an excellent cleanser for copper and brass, but like all chemical solvents for tarnishes, should be removed by washing as soon as the metal is clean.

*Benzine* and aromatic benzene are valuable constituents of liquid polishes, since they act as general solvents.

*Potassium cyanide* is used in the trade, but as it is a violent poison its use is inadvisable in the home.

*Pastes.*—These contain pulverized mineral material made into paste form with soap, and in some cases small

amounts of oxalic acid, glycerol, or a hydrocarbon. Their action is principally abrasive, and the mineral substances they contain are those found in the cleaning powders described below.

*Powders.*—Efficient polishing powders are whiting, clay, rouge, talc, quartz, emery, and silica.

*Whiting* is finely pulverized chalk. It costs about 10 cents per pound, and is useful for cleaning silver, nickel, porcelain, and glass. A mixture of whiting with water or alcohol is effective for window cleaning. One of the scouring preparations on the market is essentially a mixture of whiting and soap.

*Clay* is of varied character and comes under different names—Tripoli, rottenstone, etc. These substances cost about 40 cents per pound, and when in finely divided condition are used for general metal cleaning. Rottenstone is frequently mixed with kerosene for this purpose.

*Rouge* is preferred by jewelers for polishing gold and silver, brass and copper. Jeweler's rouge is finely pulverized red oxide of iron, prepared by a special process, and costs about 5 cents per ounce. When mixed with water it will adhere to the surface on which it is rubbed. Some of the best metal polishes on the market are combinations of rouge, oxalic acid, and a hydrocarbon.

*Talc* is pulverized magnesium silicate, and makes a good polishing agent without danger of scratching.

*Silica, quartz and emery* come in different forms, as knife brick, scouring soaps, etc., and are especially suited to the polishing of steel and iron.

*Polishing Cloths* are made usually by impregnating soft durable fabrics with rouge, talc, rottenstone or whiting. A polishing cloth may be made at home by dipping a pile fabric or a piece of chamois into rouge mixed with water or alcohol, and drying. Some of these cloths have no mineral constituent, but polish by means of the fabric itself.

### TESTS FOR CLEANING AGENTS.

*Oxalic Acid or Oxalates.*—Make a water solution, filter, add  $\text{Ca(OH)}_2$  to filtrate. White precipitate of calcium oxalate appears.

*Benzine or Benzene.*—Odor and inflammability.

*Ammonia.*—Odor and litmus test.

*Potassium Cyanide.*—Treat with fixed alkali,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$  and  $\text{HCl}$  in order given. Prussian blue color.

*Whiting.*—Add  $\text{CH}_3\text{COOH}$ . An effervescence indicates a carbonate. Make test for calcium.

*Rouge.*—Treat with boiling  $\text{HCl}$  (conc.). If rouge is present, it will dissolve. Make iron test with  $\text{NH}_4\text{SCN}$ .

*Clay.*—Will remain insoluble when treated with water or acid.

**Bleaches, Grease and Stain Removers.**—Many proprietary compounds are sold for these purposes. On analysis, the bleaches are generally found to be calcium hypochlorite, Javelle water, hydrogen and sodium peroxides, oxalic acid, or potassium permanganate, alone or in combination. Some description of the use and effect of these compounds is given in Chapter XIV. If the kind of bleach required is known, it can be bought directly, and at less expense than if purchased under its proprietary name. For example, ink eradicators usually consist of Javelle water or a solution of bleaching



powder, accompanied by an acid—oxalic, muriatic, or citric—the two being combined at the time of application.

The non-inflammable solvents for grease, familiar to the public, have for the most part carbon tetrachloride as their principal ingredient, with varying combinations of benzine or gasoline, benzene, acetone, or chloroform. They have a great advantage as to safety over the dangerous gasoline or benzine, often used carelessly in the home. These grease solvents will remove fresh paint or varnish stains, since they attack the fatty constituent in the compound. Turpentine or amylacetate also soften and dissolve dried paint and varnish.

**Bluings.**—The character of the bluing used in the laundry is of importance to the housewife. The three types in common use—solid, liquid, and aniline blues—are markedly different in properties.

*Solid blues* are now commercially prepared ultramarine blues, the former type, indigo blue, being little used at present. Ultramarine is found in nature in small quantities as lapis lazuli; as manufactured, it is a mixture of sodium and aluminium silicates, and sodium sulphide. It is characterized by insolubility in water, but the suspension of its fine particles in the bluing water gives a good blue color. Unfortunately, unless care is used, larger particles sometimes settle on the clothes, and produce blue spots.

#### TEST.

Ultramarine blue is decolorized on addition of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ . Sulphur is precipitated and  $\text{H}_2\text{S}$  evolved.

*Liquid Blues.*—These are principally Prussian blue, *i. e.*,  $\text{Fe}_4[\text{Fe}(\text{Cn})_6]_3$ . Prussian blue decomposes in the presence of an alkali, such as caustic soda, and gives a brown residue of ferric hydroxide. This may happen if soap is carried over into the bluing water. In that case the ferric hydroxide becomes iron rust on the clothes, when the hot iron is applied.

#### TEST.

Warm the sample of liquid bluing with NaOH. A brown precipitate appears if the bluing has an iron base. Filter, dissolve residue in hot dilute HCl and make test for ferric compound, with  $\text{NH}_4\text{SCN}$ .

*Aniline Blues.*—These are used less in the household than in commercial laundries, but can be procured in powder form at a laundry supply establishment. They are cheaper than other forms of bluing, as 1 ounce of the powder will make a strong solution in a gallon of water. Acids are used in most laundries for the best development of the color on the clothes. If an acid is used, it should be acetic, which is volatile and harmless, rather than oxalic, which is destructive to most fabrics.

#### TEST.

Aniline blues slowly lose color in the presence of caustic soda.

## CHAPTER XVI.

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### VOLUMETRIC AND GRAVIMETRIC ANALYSIS.

**Normal Solutions.**—The basis of volumetric analysis is the normal solution. A normal solution is one which contains the hydrogen equivalent of the substance in grams, in 1 liter of solution. For all monobasic acids and alkalies the hydrogen equivalent corresponds with the molecular weight of the compounds; for dibasic substances it is one-half of the molecular weight. In similar manner tri- and tetrabasic bodies have hydrogen equivalents corresponding to one-third and one-quarter of their molecular weight. To find the equivalent of a salt, refer back to the acid from which the salt is made. For example,  $\text{Na}_2\text{CO}_3$  is the sodium salt of  $\text{H}_2\text{CO}_3$ , therefore it is dibasic, and its normal solution would contain one-half its molecular weight, or 53, in grams per liter.

Equal volumes of normal solutions of different substances are of equal strength, and equal volumes of normal acid and alkali solutions neutralize each other.

Normal solutions may be made one-tenth or one-hundredth of their full strength, either by taking the corresponding fractions of their respective equivalents or by diluting the full normal solutions proportionately; they are known as deci- and centi-normal solutions respectively.

To explain the preparation of the normal solutions of acid and alkali, one example from each class will suffice,

and as hydrochloric acid and caustic soda have the most extensive application, their preparation will be given.

**Preparation of N/HCl.**—The molecular weight of HCl is 36.5, therefore 36.5 grams per liter are needed, but as it is a volatile liquid and cannot be weighed with any accuracy, it is usual to calculate the volume of the liquid from its specific gravity, and to measure out the result in cubic centimeters, allowing a little for loss. Using

the formula  $\frac{W}{D} = V$ , the calculation is simple and is

made as follows: divide the equivalent in grams (36.5) by the specific gravity of the concentrated acid (1.2); this gives 30.4+ as a quotient and is the number of cubic centimeters to be used if the acid were 100 per cent. strength, but the strongest acid is only 40 per cent., hence this quotient must be multiplied by 2.5 ( $30.4 \times 2.5 = 76$  cc.). It is safe to take 78-80 cc., adding it to 300 or 400 cc. of distilled water and when cool diluting to exactly 1 liter.

The solution must now be standardized against a normal solution of an alkali which can be made exact. Sodium carbonate, the equivalent of which is 53, can be obtained of a high degree of purity and may be weighed exactly. It is hardly necessary to make up a large quantity, so that 5.3 grams of pure *dry* soda are usually weighed accurately, dissolved in the least quantity of water and the resulting solution diluted to exactly 100 cc. at or about 60° F. This constitutes the exact normal soda, 1 cc. of which contains 5.3 milligrams of soda.

Measure 10 cc. of the soda very exactly with a pipette, run it into a small beaker containing about 100 cc. of distilled water and add 2 or 3 drops of methyl orange solution. Fill a burette with the acid solution. Note the level, and run it, drop by drop, with constant stirring, into the soda. Stop when the last drop changes the color from yellow to pink which remains even after stirring for some moments. Read the burette and note the number of cubic centimeters, and fractions used. Say the quantity is 9.8 cc., indicating that this quantity contains as much acid as should exist in 10 cc.; consequently, 980 cc. of the liquid should be diluted to 1 liter. If the total amount of acid is less, calculate what bulk it should occupy and dilute accordingly. Continue the titration until equal volumes of acid and alkali exactly neutralize each other.

The acid keeps well, but should be preserved in tightly stoppered glass bottles to prevent evaporation.

**Preparation of N/NaOH.**—The caustic soda is deliquescent and absorbs carbon dioxide, so must be weighed rapidly and approximately, using rather more than the 40 grams required, say 50 grams. This is dissolved in 300 or 400 cc. of water, cooled and diluted to 1 liter. Draw off 10 cc. of the normal acid in a pipette, allow it to run into a small beaker containing about 100 cc. of distilled water, and add a few drops of phenolphthalein. Fill a clean, dry burette with the caustic soda. Note its level and run it, drop by drop, with constant stirring, into the acid solution until a faint but distinct pink tint

remains after stirring for some moments. Read off the quantity used, say 9.5 cc., showing the solution to be too strong and requiring dilution as in the case of the acid. After performing this operation the acid and the alkali should be correct and 1 cc. of one will exactly neutralize an equal quantity of the other.

**Use of Indicators.**—A change in a solution from acidity to alkalinity, or the reverse, can be shown by certain color substances or indicators, sensitive to the slightest excess of acid or alkali.\* The indicators in common use in acidimetry and alkalimetry are phenolphthalein and methyl orange. The work of an indicator may be illustrated by the action of phenolphthalein, a weak acid which undergoes little dissociation in solution. In the non-ionized state it is colorless. If, however, its acid solution is neutralized by an alkali, a slight excess of the alkali forms a salt of phenolphthalein which ionizes with a deep red color. A strong base is necessary in order to give a sharp reaction. Ammonia, for instance, is too weak a base to ionize the weakly acid phenolphthalein in dilute solution. Phenolphthalein is used most frequently as an indicator for weak acids (excepting carbonic and hydrosulphuric) titrated against normal sodium hydroxide.

Methyl orange, on the other hand, is red in its molecular state, and changes to yellow on dissociation. It is a moderately strong acid, and if added to a basic solution the salt formed is yellow, but the addition of a

\* For Theory of Indicators, see Ostwald: *Foundations of Analytical Chemistry*, and Cairns: *Quantitative Analysis*.

slight excess of a strong acid is sufficient to produce the red color of the non-ionized substance. Its reaction with weak acids is not sharp, so its use is not advised in connection with organic acids. Because of its strongly acid nature methyl orange is useful in titrating against weak bases. It must always be used in cold solution, and in small amounts.

Congo red and rosolic acid are usually employed in the Kjeldahl determination of nitrogen. The former is blue in acid solution, red in alkaline. It is dissolved in water for use, and only small amounts should be taken. Rosolic acid is yellow in the presence of acids; cherry red with alkalis. It is dissolved in 50 per cent. alcohol for use.

**To test unknown substances,** first determine the compound present by qualitative analysis, and then weigh or measure some convenient quantity, dissolve or dilute with distilled water, add the indicator and run in the acid or the alkali until the neutral point is reached. Observe the number of cubic centimeters used, multiply each by its value in milligrams of the substance sought, and divide the result by the quantity used; multiplying this quotient by 100 will yield per cent.

Value of 1 cc. of normal soda in each of the following:

Sodium carbonate .....	0.053
Acetic acid .....	0.060
Lactic acid .....	0.090
Tartaric acid .....	0.075
Citric acid .....	0.064
Hydrochloric acid .....	0.0365

Nitric acid .....	0.063
Sulphuric acid .....	0.049
Potassium hydroxide .....	0.056
Ammonium hydroxide .....	0.035
Calcium hydroxide .....	0.037

*For example*, to neutralize 10 cc. of a solution of acetic acid of unknown strength, 8 cc. of N/NaOH are required. The calculation would be:

1 cc. N/NaOH = 0.06 gram acetic acid.

8 cc. N/NaOH were used.

$8 \times 0.06 \text{ gram} = 0.48 \text{ gram acetic acid in 10 cc.}$

$100 \times (0.48 \div 10) = 4.8 \text{ grams acetic acid in 100 cc.}$

$\therefore$  the strength of the acid is 4.8 per cent.

#### APPLICATIONS OF VOLUMETRIC ANALYSIS.

**Analysis of Vinegars.**—Take the specific gravity of the sample. Decolorize a portion (50-100 cc.) by passing it through a bone-black filter, rejecting the first funnel full. Take 10 cc. of the product, dilute with a convenient bulk of water (about 50 cc.), add 1 or 2 drops of phenolphthalein as indicator, and titrate against N/NaOH. Calculate as acetic acid, using the specific gravity of the vinegar to check the resulting per cent. Example:

Specific gravity of sample may be 1.014,  $\therefore$  weight of 10 cc. = 10.14 grams.

Amount of acetic acid found in 10 grams may be 0.534 gram.

$\therefore 0.534 \div 10.14 = 5.26$ , the per cent. of acetic acid in the sample.

*To distinguish the source of vinegar*, evaporate 10 cc. to dryness, and note the odor. Cider vinegar will give an odor suggesting baked apples; malt vinegar, a malt odor; distilled vinegar, a sharp acid odor. Ignite at a low temperature to light-colored ash. In the case of genuine cider or wine vinegars the quantity



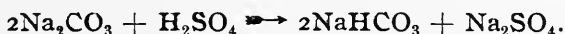
of ash is comparatively large and the reaction will be alkaline. Synthetic vinegar will leave no appreciable residue.

*Test for Free Mineral Acids.\**—Dilute 5 cc. of the vinegar with 5 to 10 cc. of water to reduce the acidity to about 2 per cent. of acetic acid, and add 4 or 5 drops of a solution of methyl violet (1 part of Methyl Violet 2B, No. 56 of Bayer Farbenfabrik, Elberfeld, in 10,000 parts of water). Mineral acids change the blue violet color to a blue green or green.

*Test for Phosphoric Acid.*—Burn to ash in the presence of a few drops of  $\text{HNO}_3$  and make the usual test for phosphoric acid.

*Baking Soda—Test for Purity.\*\**—Ordinary baking soda may contain some  $\text{Na}_2\text{CO}_3$ . To determine the percentage of  $\text{NaHCO}_3$  in the sample, dissolve 1 gram of commercial  $\text{NaHCO}_3$  in 100 cc. of distilled water, add 2 drops of methyl orange, and titrate against  $\text{N}/10 \text{H}_2\text{SO}_4$ . Since the freed carbonic acid is too weak an acid to produce the red color with methyl orange, the latter will give the end point of titration in this case only when the  $\text{N}/10 \text{H}_2\text{SO}_4$  has neutralized the total alkalinity (combined as mono- and bicarbonate) of the soda.

Now dissolve another gram of the sample in 250 cc. of cold water, add phenolphthalein, and titrate with  $\text{N}/10 \text{H}_2\text{SO}_4$ . The nose of the burette should dip into the solution, which should be well stirred during the titration. No carbonic acid should escape from the liquid during the operation. Under suitable conditions of dilution and temperature the reaction is:



Therefore, 1 cc. of half-normal sulphuric acid equals 0.106 gram of  $\text{Na}_2\text{CO}_3$  present.

The difference between the amounts of  $\text{N}/10$  acid used in the two titrations is the measure of the bicarbonate of soda in the sample.

*Cream of Tartar—Test for Purity.*—Weigh 1 gram of cream of tartar, add 100 cc. of distilled water, and 2 drops of phenol-

\* From Sherman's *Organic Analysis*.

\*\* Cairns: *Quantitative Analysis*.

phthalein. Run in  $N/\text{NaOH}$  until the pink color comes. (A certain amount of the alkali is necessary to the complete solution of the cream of tartar.) Now add  $N/10$   $\text{HCl}$  drop by drop until the color just disappears, and subtract the amount used from the alkali in terms of tenth-normal. The difference is the amount of  $\text{NaOH}$  required to neutralize the cream of tartar. Calculate the percentage of cream of tartar in the sample.

*Household Ammonia.*—Take the specific gravity of the sample, and dilute 10 cc. with a convenient bulk of distilled water. Add 2 drops of methyl orange, and titrate against  $N/\text{HCl}$ . Calculate percentage strength, using the specific gravity as a factor.

**Analysis of Soap or Soap Powder.**—In a 3-inch porcelain dish place 1-2 teaspoonfuls of clean dry sand and a small glass stirring rod; weigh the whole. Add 2-3 grams of the soap sample, finely shaved, and enough 95 per cent. alcohol to cover the material. Evaporate over a water bath, stirring meanwhile, until the alcohol is evaporated. Dry the contents of the dish in an air bath at  $105^\circ$  to constant weight. Estimate the loss in weight as water.

Weigh another gram of the sample, finely shaved, and heat for 2-2½ hours in an air bath, at  $105^\circ$ . Treat the dried material on a hot water bath with successive portions of hot neutral 95 per cent. alcohol, using about 50 cc. at a time and 400-500 cc. in all. Decant each portion of the solution through a balanced filter paper, finally washing the last portion through the filter with additional alcohol. The combined filtrates contain the dissolved soap; the residue on the filter paper is carbonates, chlorides, borates, etc., and insoluble mineral matter. Proceed with residue and filtrate as follows:

1. *Residue.*—Treat filter paper with boiling distilled water until all trace of alkalinity or residue in the last 2 or 3 drops of the filtrate has disappeared. Dry the paper in the air bath for about an hour and calculate weight of insoluble material remaining on it. Examine this under a magnifying lens for the presence of glistening particles of pulverized quartz, etc. Make up the water extract of the soluble material to bulk (*c. g.*, 500 cc.), take 100 cc.

and determine total alkalinity by titrating against  $N/H_2SO_4$ . Calculate as  $Na_2CO_3$ . In another 100 cc. calculate chlorides by first exactly neutralizing with dilute  $HNO_3$ , then titrating with  $N/10 AgNO_3$ . Use potassium chromate as indicator. Calculate that 1 drop of  $N/10 AgNO_3$  is equivalent to 0.000293 gram sodium chloride. Concentrate a third portion to one-tenth bulk, and make a qualitative test for borax as follows: Exactly neutralize with dilute  $HCl$ , immerse a strip of freshly prepared turmeric paper in the liquid, and dry at warm water heat. Make a second test for borax on another portion, by boiling down until all of the watery liquid has disappeared, cooling, adding a mixture of equal parts of alcohol and glycerol, and applying a flame. If the mixture burns with a yellow flame bordered with green, borax is present.

Evaporate the balance of the solution to dryness, heating finally to  $110^\circ$ , take up with a little water and a few drops of  $HCl$ , and test for sulphates and silicates.

2. *Filtrate*.—Heat on a water bath until the odor of alcohol has disappeared, keeping the solution up to full amount by additions of water. Cool, bring solution up to bulk, and determine free alkali ( $NaOH$ ) by titration against  $N/H_2SO_4$ . Then add a known excess of the normal acid (*e. g.*, 5 cc.), boil until clear, add a weighed quantity (about 5 grams) of white wax, and melt. Allow the mixture to stand undisturbed until the wax hardens, remove the cake, press it between filter papers to remove all moisture, and when dry weigh. The increase in weight is due to fatty acids. Titrate the solution against  $N/NaOH$ . The difference between the 5 cc. of  $N/H_2SO_4$  added at the beginning and the result now obtained gives the combined alkali. It should amount to about one-seventh the weight of the fatty acids. Take the sum of the weights of combined alkali and fatty acids as the measure of the soap present in the sample.

Report in percentages the findings of water, carbonates, chlorides, free and combined alkali, fatty acids, and insoluble matter.

**Test for Naphtha Soap.**—Make a strong water solution of the soap sample in a small flask, acidify slightly with diluted  $\text{H}_2\text{SO}_4$ , and distill the mixture at as low a temperature as possible. If any hydrocarbon is present it will pass over and condense with the watery vapor. Note the odor.

For the detection of rosin or rosin oil in soap see the *Liebermann-Starch Reaction*, *Sherman's Organic Analysis*.

**Analysis of a Cereal.**—The process consists in the determination of water, ash constituents, protein, fat, and carbohydrate.

1. *Water.*—Dry 1-2 grams of the powdered cereal to constant weight, at not over  $105^\circ$ . Calculate percentage of water, and use figures obtained in correcting subsequent determinations of other constituents.

2. *Ash Constituents.*—Ignite 5 grams of the material in a muffle furnace at the lowest possible heat to char the material thoroughly. Cool, and make hot water extract of soluble alkaline salts. Separate by filtration and evaporate the liquid. Dry the charred residue and ignite to white or light-colored ash. Cool and add the water extract and evaporate to dryness. Weigh; the result is total ash. Test the ash qualitatively in the ordinary manner for its constituents.

*Protein.*—Weigh 1-2 grams of the sample, place in a Kjeldahl flask, add 20 cc. of concentrated sulphuric acid, 10-12 grams of potassium sulphate, and 0.5 gram of copper sulphate. Partly close the neck of the flask with a small funnel for purposes of condensation, and heat under a hood, gently at first and then strongly, until the mixture is colorless. It is well to continue heating for 15-30 minutes after this stage is reached. The nitrogenous matter in the cereal has been converted into ammonium sulphate by the acid of the sulphuric acid. The process now consists in liberating ammonia from this by the addition of

caustic soda, distilling the free ammonia into a known amount of sulphuric acid, and calculating the amount of nitrogen present.

Proceed by cooling the material in the Kjeldahl flask, adding about 250 cc. of distilled water, and after the solid matter has dissolved, 4 or 5 drops of rosolic acid. Put 100 cc. of N/10  $\text{H}_2\text{SO}_4$  and a few drops of Congo red in an Erlenmeyer receiving flask, and arrange to connect distilling and receiving flasks with a water condenser. The delivery tube of the condenser should reach below the acid in the receiving flask. Place small pieces of zinc and paraffin in the Kjeldahl flask to prevent bumping, add 80 cc. or more of caustic soda (about  $38^\circ$  Bé.) and connect up at once. Distill over a low flame at first, later increase the heat, until about half the contents of the flask have passed over. If the color in the receiving flask becomes red, showing an excess of ammonia, quickly add a measured additional amount of the N/10  $\text{H}_2\text{SO}_4$ . Titrate the excess of acid in the flask against N/10 NaOH and calculate that 1 cc. of N/10  $\text{H}_2\text{SO}_4$  is the equivalent of 0.0014 gram nitrogen. As the average percentage of nitrogen in protein material is approximately 16, the grams of nitrogen found multiplied by the factor 6.25 will give the amount of protein in the sample.\*

*Fat.*—Weigh 1-2 grams of the air-dried, pulverized material, place in an extraction thimble, and introduce into a Soxhlet or other approved form of extraction apparatus. Extract with a pure form of ether into a tared flask. The duration of the extraction depends on the character of the material, but 16 to 24 hours are usually allowed.

Remove the flask, evaporate the ether, weigh, and calculate amount of extract.

*Carbohydrate.*—Determine carbohydrate by difference. If the cereal has a notable amount of soluble carbohydrate, make a water extract, invert and estimate reducing sugar, and determine the insoluble carbohydrate by difference. Use the following method:

\* For modifications of the Kjeldahl method see Sherman: *Organic Analysis*.

**Estimation of Reducing Sugars.**—Mix 15 cc. of Fehling's solution A with the same amount of Solution B in an Erlenmeyer flask of about 250-300 cc. capacity, add about 50 cc. of freshly boiled distilled water, and heat in boiling water for 5 minutes. Measure with a pipette 25 cc. of the sugar solution, which should be of such a strength as not to contain more than 0.5 gram of reducing sugar. Add this to the Fehling's mixture and place the flask in boiling water for 15 minutes. Remove, filter at once with the aid of moderate suction through a Gooch crucible prepared with asbestos.\* If the filtrate is not distinctly blue, showing that an excess of Fehling's has been used, the operation must be repeated with a more dilute solution of the reducing sugar. Wash the precipitate of cuprous oxide with boiling distilled water until the filtrate is no longer alkaline. The cuprous oxide can now be (1) washed with alcohol and then with ether, dried in an air bath at 100° for 20 minutes, weighed as cuprous oxide, and calculated to its cupric oxide equivalent. The corresponding weight of reducing sugar may then be determined by referring to Defren's table (see Sherman: *Organic Analysis*).

\* To prepare the Gooch crucible for gravimetric determination of cuprous oxide, proceed as follows: Boil a good quality of asbestos with nitric acid (specific gravity 1.05 to 1.10), wash with water, boil with 25 per cent. sodium hydroxide, wash, and repeat the treatment. Finally stir the washed asbestos with water, pour some into a Gooch crucible, and draw it into place with moderate suction. When a tight felt about 1 centimeter thick has been laid down, ignite to constant weight and record weight of crucible and asbestos. Test by running through it a "blank" of hot alkaline Fehling's solution and washing with water as in a regular determination. The loss in weight should not exceed  $\frac{1}{2}$  milligram. If it does, the filter is again treated with acid and alkali until it ceases to lose in weight. The crucible may be used for successive determinations by dissolving the precipitate each time with nitric acid, washing, igniting to constant weight.

Or (2) the cuprous oxide may be ignited and weighed as cupric oxide and the corresponding amount of reducing sugar found as before. A third method consists in determining the copper by electrolysis (see Allihn's method and table for the determination of dextrose).

# CHAPTER XVII.

## REAGENTS.

Commercial forms	Laboratory strength						
	Sp. gr.	Per cent.	Concentrated	Sp. gr.	Dilute		Sp. gr.
					Vols. H <sub>2</sub> O	Vols. acid	
<i>Acids</i>							
HCl .....	1.2	40	full strength	1.2	1	1	1.1
			Vols. H <sub>2</sub> O   Vols. acid				
HNO <sub>3</sub> .....	1.4	70	1   1	1.2	3	1	1.1
H <sub>2</sub> SO <sub>4</sub> .....	1.84	94	full strength	1.84	7	1	1.1
CH <sub>3</sub> COOH .	1.06	50	full strength	1.06	10	1	1.007
					Vols. H <sub>2</sub> O	Vols. alk.	
<i>Alkalies</i>							
NH <sub>4</sub> OH ....	0.9	28	full strength	—	1	1	0.945
NaOH .....	—	—	20 per cent.	1.3	10 per cent.		1.14
KOH .....	—	—	20 per cent.	1.23	10 per cent.		1.1
<i>Salts</i>							
Na <sub>2</sub> CO <sub>3</sub> ....	—	—	dry	—	10 per cent.		1.1
BaCl <sub>2</sub> .....	—	—	—	—	10 per cent.		—
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	—	—	—	—	saturated		—
Na <sub>2</sub> HPO <sub>4</sub> ....	—	—	—	—	saturated		—
NH <sub>4</sub> Cl .....	—	—	—	—	10 per cent.		—
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .	—	—	dry	—	saturated		—
NH <sub>4</sub> SCN ...	—	—	—	—	5 per cent.		—
NaCl .....	—	—	dry	—	saturated		1.2
MgSO <sub>4</sub> . ...	—	—	dry	—	saturated		—
HgCl <sub>2</sub> .....	—	—	—	—	saturated		—
Tannin ....	—	—	—	—	20 per cent.		—
AgNO <sub>3</sub> .....	—	—	—	—	5 per cent.		—
Co(NO <sub>3</sub> ) <sub>2</sub> ..	—	—	—	—	10 per cent.		—
K <sub>4</sub> Fe(CN) <sub>6</sub> .	—	—	—	—	10 per cent.		—

### Special Reagents.

*Ammonium Molybdate*, (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>.

Dissolve 100 grams MoO<sub>3</sub> in 200 cc. strong NH<sub>4</sub>OH



and 200 cc.  $\text{H}_2\text{O}$ ; slowly pour resulting solution in 1,500 cc.  $\text{HNO}_3$  specific gravity 1.2.

*Magnesia Mixture.*

1 gram  $\text{MgSO}_4$  or  $\text{MgCl}_2$ , 1 gram  $\text{NH}_4\text{Cl}$ , 4 cc. ammonia, 8 cc. water.

*Millon's Reagent.*—100 grams mercury dissolved in 71.5-72 cc.  $\text{HNO}_3$  specific gravity 1.4 in the cold, when action ceases add twice the volume of cold water.

*Fehling's Reagent.*—Solution A—34.64 grams  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 400 cc. of cold water, when dissolved make up to 500 cc.

Solution B—50 grams  $\text{NaOH}$  + 180 grams  $\text{NaKC}_4\text{H}_4\text{O}_6$  in 300 cc. of water, when dissolved and cooled make up to 500 cc.

For use mix equal volumes of A and B and add two volumes of water.

*Barfoed's Reagent.*—4.0 grams copper acetate, 100 cc. water, 2 cc. acetic acid.

*Nylander's Reagent.*—Two grams bismuth subnitrate, ( $\text{BiONO}_3$ ), and 4 grams of Rochelle salt, ( $\text{NaKC}_4\text{H}_4\text{O}_6$ ), in 100 cc. of 8 per cent.  $\text{NaOH}$ , specific gravity 1.08.

*Nessler's Reagent.*—35 grams of  $\text{KI}$  and 13 grams of  $\text{HgCl}_2$  in 800 cc.  $\text{H}_2\text{O}$ . Heat below boiling until dissolved, add immediately a cold saturated solution of  $\text{HgCl}_2$  until the red precipitate fails to dissolve after stirring. Cool and add 160 grams  $\text{KOH}$  dissolved in as little water as possible, and make up to 1 liter. After standing 24 hours pour off the clear liquid and reserve

for use. If necessary, add a little more (3—5cc.)  $\text{HgCl}_2$  to increase the sensitiveness. When properly prepared, the solution has a pale yellow color.

*Gries's Reagent for Nitrites.*—Dissolve 1 gram of sulphanilic acid in 300 cc. of acetic acid specific gravity 1.04 (30 per cent.).

Boil 0.2 gram of  $\alpha$ -naphthylamine in 400 cc. of distilled water, filter through a plug of washed absorbent cotton and add 360 cc. of acetic acid (30 per cent.).

To dilute 50 per cent. acid to 30 per cent., take  $\frac{3}{5}$  of 100 or 60 cc. of acid and dilute to 100 cc.

*Basic Acetate of (Sugar of) Lead Solution.*—Boil 232 grams of lead acetate and 132 grams of litharge ( $\text{PbO}$ ) in 750 cc. of distilled water for half an hour, cool dilute to one liter. Allow liquid to stand until clear and decant. Specific gravity of solution should be about 1.267.

*Alumina Cream for Clarifying Syrups, Etc.*—Precipitate a solution of alum with slight excess of ammonia, wash by decantation or filtration until neutral and suspend in water to a creamy consistency.

*Meta Phosphoric Acid.*—Dissolve glacial phosphoric acid ( $\text{HPO}_3$ ) or phosphoric anhydride,  $\text{P}_2\text{O}_5$ , in ice and water. As the solution rapidly changes to  $\text{H}_3\text{PO}_4$  make it fresh for each day's work.

*Alcohol.*—95 per cent. is always acid, neutralize with dilute alkali before using. Alcohol may readily be recovered from solutions and wash liquids by distilling over hot water at  $78^\circ$ – $80^\circ$ .

*Ammonium Sulphide.*—Mix equal volumes of distilled water and strong ammonia (specific gravity 0.9); divide the resulting solution in equal parts. Pass a current of  $H_2S$  through one-half the solution until saturated and then add the balance of the dilute ammonia.

*Alkaline Pyrogallol.*—Dissolve 20 grams of the best pyrogallol in 100 cc. of cooled freshly boiled distilled water, add 0.5 cc. of concentrated  $H_2SO_4$ . This solution keeps well.

For use take enough of the above and make strongly alkaline with 10 per cent.  $NaOH$ . Avoid contact with air and use immediately.

*Alkaline Potassium Permanganate.*—8 grams of crystallized potassium permanganate with 200 grams of caustic potash or a corresponding amount of caustic soda, in 1 liter of water.

*Acidified Potassium Permanganate.*—0.395 gram potassium permanganate in 1 liter of water. Add 10 cc. of  $H_2SO_4$  before using.

*Alcoholic Potash.*—56 grams  $KOH$  in 1 liter 95 per cent. alcohol.

*Molisch's Reagent.*—Make a 15-20 per cent. alcoholic solution of alpha-naphthol. Use with  $H_2SO_4$  as directed.

*Schweitzer's Reagent.*—Dissolve 5 grams of copper sulphate in 100 cc. of boiling water, add caustic soda solution until the cupric hydroxide is completely precipitated, wash the precipitate well and dissolve in the least quantity of 20 per cent.  $NH_4OH$  (3 volumes ammonia specific gravity 0.9 + 1 volume  $H_2O$  = 20 per cent.).

## APPENDIX.

### Useful Tables and Equivalents.

	Per cent.	Sp. Gr.	Degrees Bé.
H <sub>2</sub> SO <sub>4</sub> .....	0.935	1.007	1
	9.584	1.066	9
	93.5 (conc.)	1.835	66
HCl .....	1.124	1.006	1
	10.17	1.05	7
	20.00	1.1027	13.5
	40.55	1.2033	24.5
NaOH.....	1.2	1.014	2
	10.06	1.116	15
	11.84	1.134	17
	20.59	1.231	27
	24.81	1.274	31
	32.47	1.357	38

$$1 \text{ gram} = \begin{cases} 15.432 \text{ grains} \\ 0.0353 \text{ oz.} \\ 0.0022 \text{ lb.} \end{cases}$$

$$28.35 \text{ grams} = 1 \text{ oz.}$$

$$453.6 \text{ grams} = 1 \text{ lb.}$$

$$1 \text{ kilogram} = 2.2 \text{ lbs.}$$

$$1 \text{ teaspoon} = 5 \text{ cc.}$$

$$1 \text{ tablespoon} = 15 \text{ cc.}$$

$$1 \text{ cup} = 16 \text{ tablespoons}$$

$$2 \text{ cups} = 1 \text{ pint}$$

$$1 \text{ liter} = 1.057 \text{ qt. (U. S.)}$$

$$1 \text{ inch} = 2.54 \text{ cm. or } 0.0254 \text{ meter}$$

$$1 \text{ foot} = 30.48 \text{ cm. or } 0.3048 \text{ meter}$$

Method of changing from a stronger to a weaker solu-

tion, *e. g.*, from acetic acid of 50 per cent. strength to 20 per cent.:

$$20 \text{ per cent.} : 50 \text{ per cent.} :: 100 \text{ cc.} : x \text{ cc.}$$

$$x = 250 \text{ cc.}$$

Therefore make up 100 cc. of the 50 per cent. acetic acid to 250 cc.

Interchange of Centigrade and Fahrenheit degrees:

$$F = \frac{9}{5} C + 32 \qquad C = \frac{5}{9} (F - 32).$$

Comparison of Fahrenheit and Centigrade degrees:

Fahr.	Cent.	Fahr.	Cent.
0	-17.78	95	35.00
32	0.00	98	36.67
40	4.44	100	37.78
41	5.00	104	40.00
50	10.00	113	45.00
59	15.00	122	50.00
65	18.33	140	60.00
68	20.00	145	62.78
72	22.22	158	70.00
77	25.00	167	75.00
80	26.67	178	80.00
		212	100.00

To convert degrees Baumé to specific gravity apply the formulas:

For liquids heavier than water—

$$\frac{144}{144 - \text{Bé}^\circ} = \text{specific gravity.}$$

For liquids lighter than water—

$$\frac{144}{134 + \text{Bé}^\circ} = \text{specific gravity.}$$

## List of Apparatus for Students in Household Chemistry.

---

Three rings (iron).	Microscope slides with cover glasses—four.
Filter ring.	Test tubes—1 doz. 6-inch
Clamps.	Test tubes—1 doz. 4-inch.
Triangular file.	Hard-glass test tubes (1 in. $\times$ 6 in.)—two.
Round file.	Graduates, 10 cc. 25 cc.
Triangles.	Porcelain dishes — two (3½ inch).
Wire gauze.	Beakers (Jaikel 1-4).
Steel forceps.	Tripod.
Wing-top.	Test tube rack.
Horn spatula.	Agate boilers with cover, ½ pint.
Tube brushes—three (assorted sizes).	4 funnels—two inch and three inch.
Filter paper.	Flasks—one 4 oz. high.
Test tube holder.	Flasks—two 4 oz. low (wide mouth).
Scissors.	Flask—one 16 oz. round bottom.
Knife.	Wash-bottle—16 oz.
Thermometer. Centigrade 0°-120°.	Wide mouth bottle, 8 oz.
Glass rod with platinum wire.	Water-bath, 5 in.
Flat glasses, 4 inch.	
Blue glass.	
Watch-crystals—four.	

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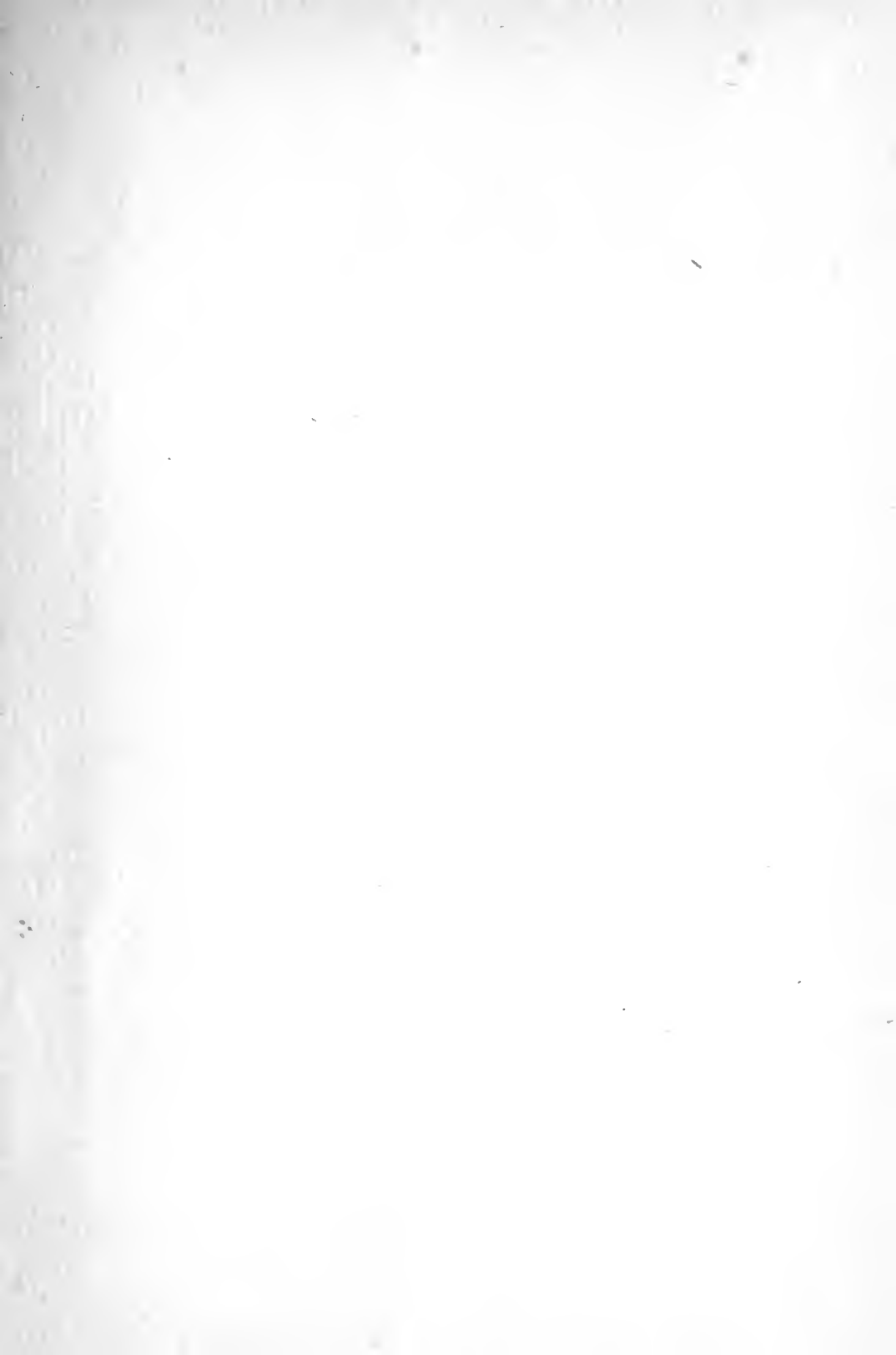
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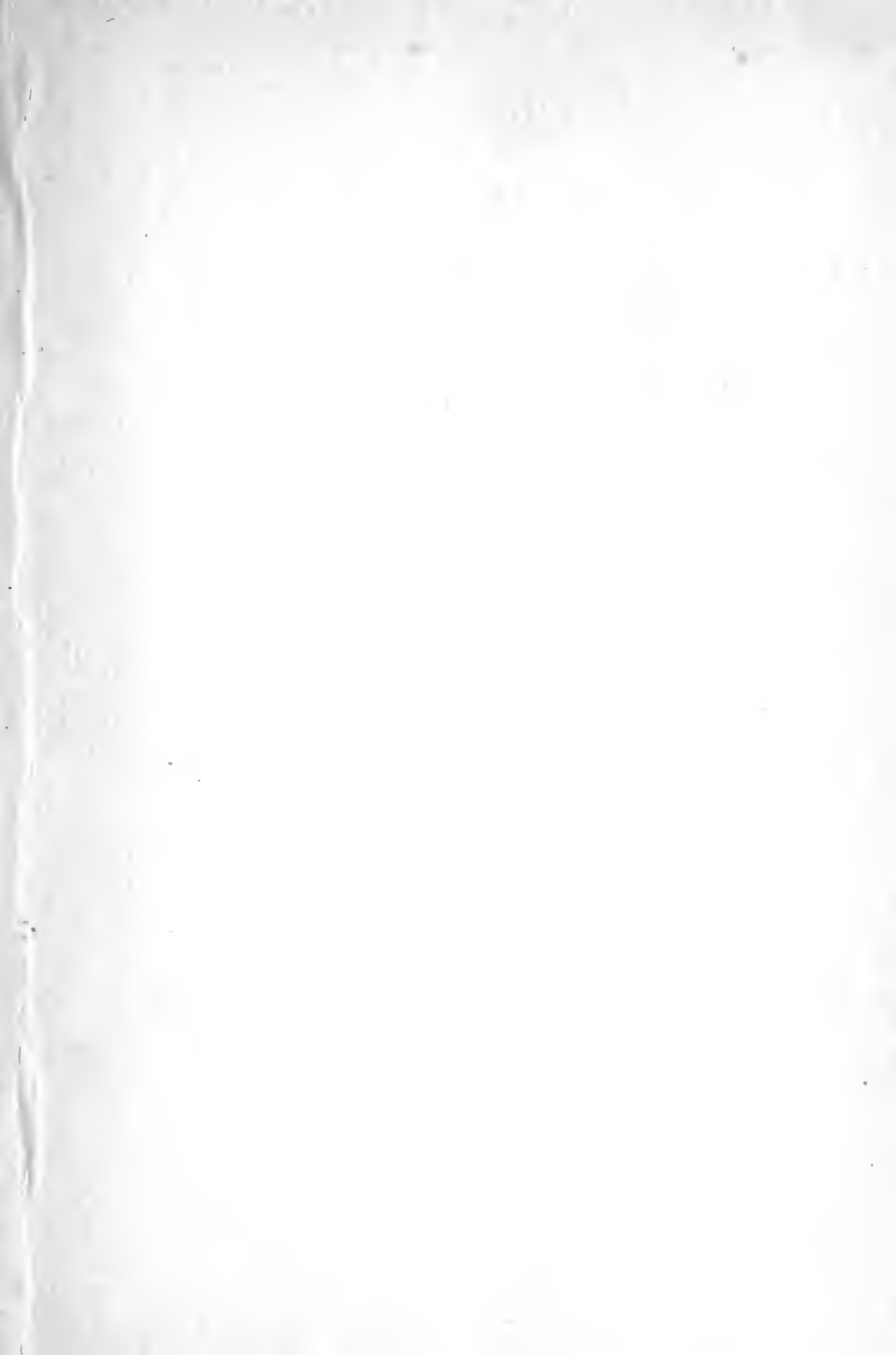












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